

Materials Transfer at the Continent-Ocean Interface under the Scenario of the Anthropocene

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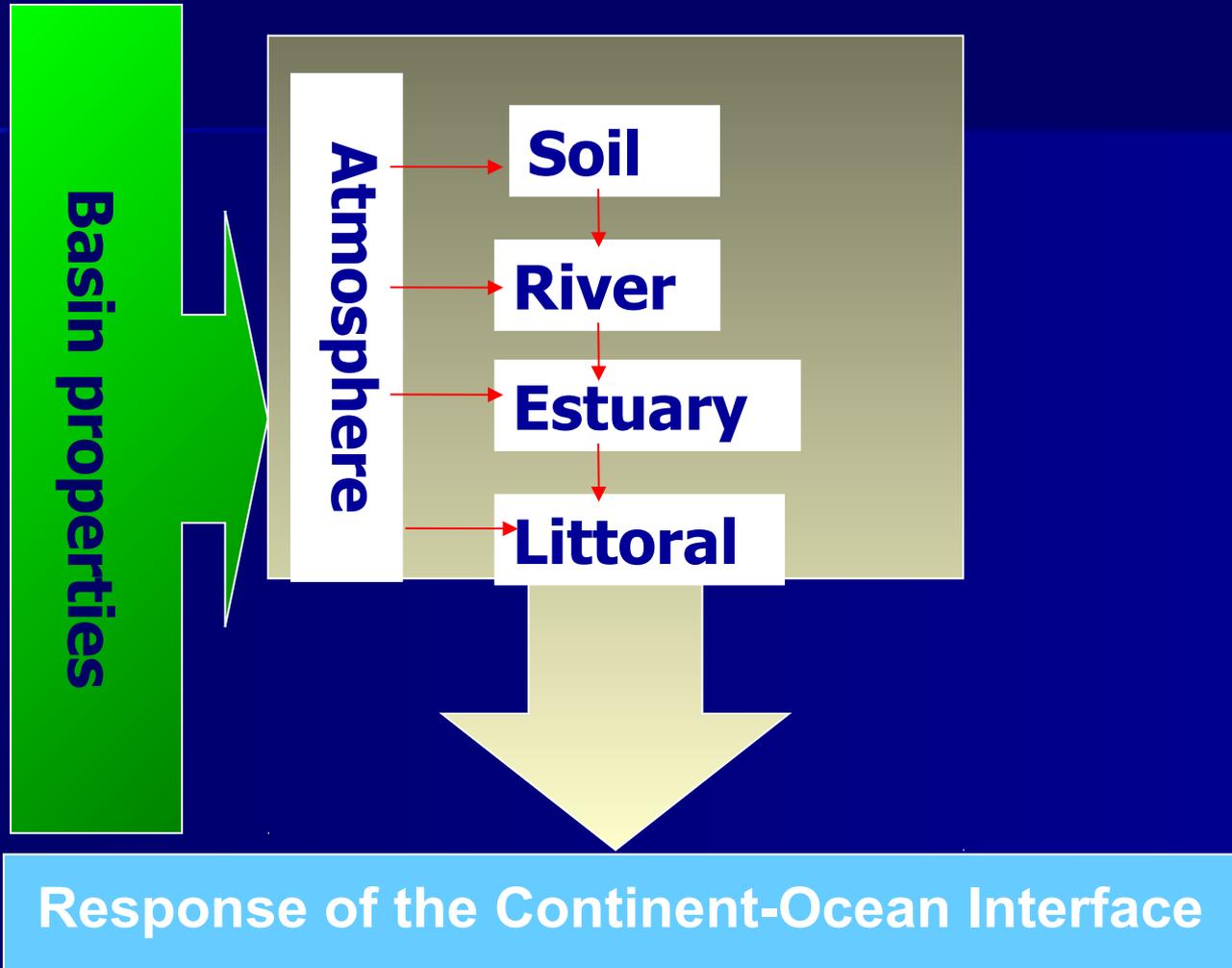


<http://inct.cnpq.br/web/inct-tmcocean/home/>

Continent-Ocean Transfer Processes *

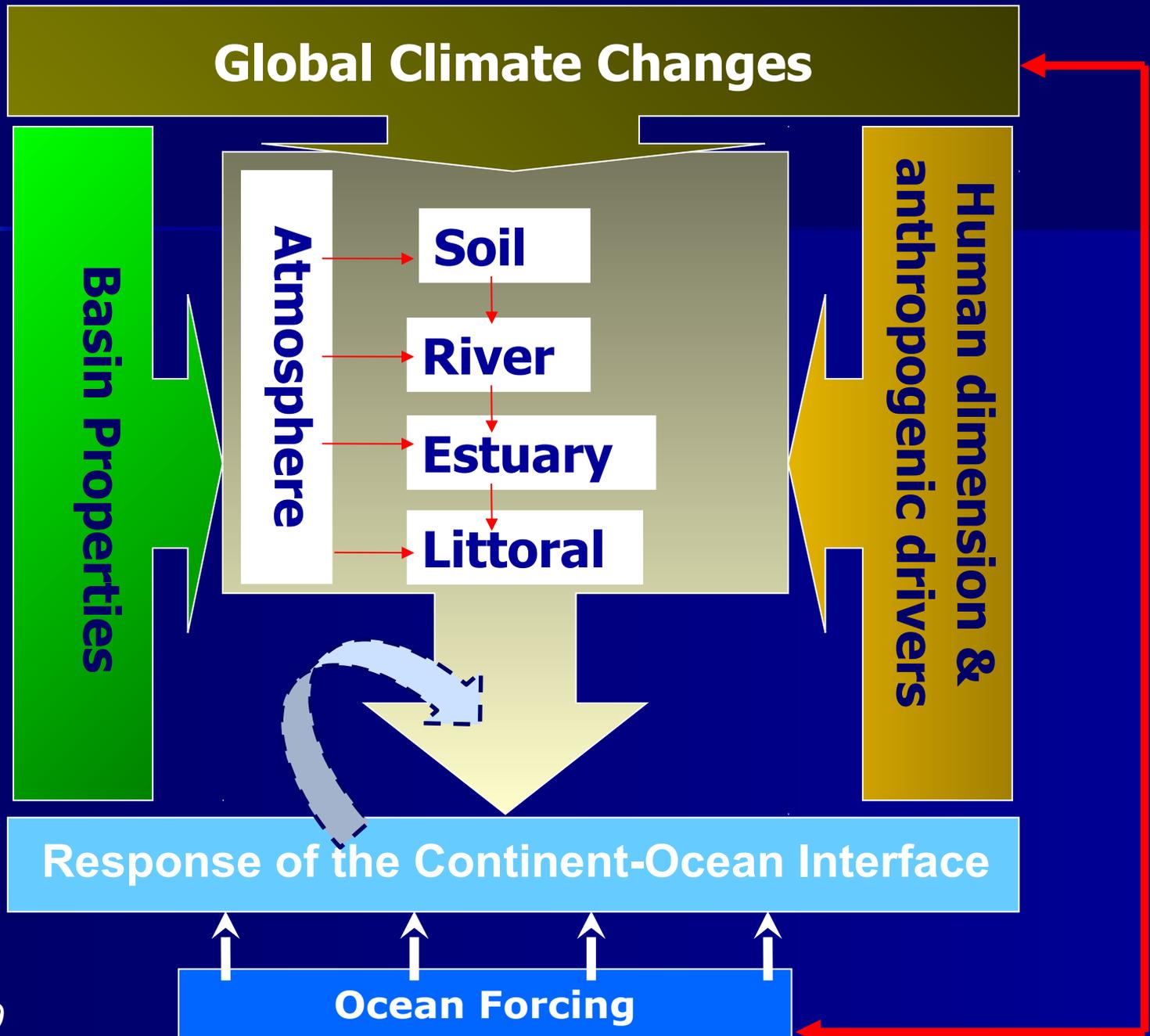
(Concepcion at the end of the 20th century)

Biogeochemistry of transfer processes



Present –day Continent-Ocean Transfer Processes *

Biogeochemistry of transfer processes



Principals characteristics of the COI

- 1 – Transfer of water, mass and energy occur through the continent-ocean interface at large spatial scale both in terrestrial and marine adjacent areas
- 2 - Transfer occurs simultaneously both at continent-ocean and ocean-continent directions at different temporal e spatial scales.
- 3 – Transfer is affected by natural and anthropogenic vectors.

c.f. Kjerfve, 2007

Vectors affecting the continent-ocean transport

Naturals: geotectonic (subsidence/elevation), wind, earthquakes, hurricanes, tsunamis, inundations, sea level oscillation, type and abundance of coastal vegetation, etc.

Anthropogenic: wastewaters, agriculture runoff, pollutant emissions and remobilization, conversion of coastal areas, engineering works, global climate changes.

Synergies: vectors act simultaneously and do affect each other, including through feedback mechanisms, in generally very poorly known.

Holocene

Anthropocene

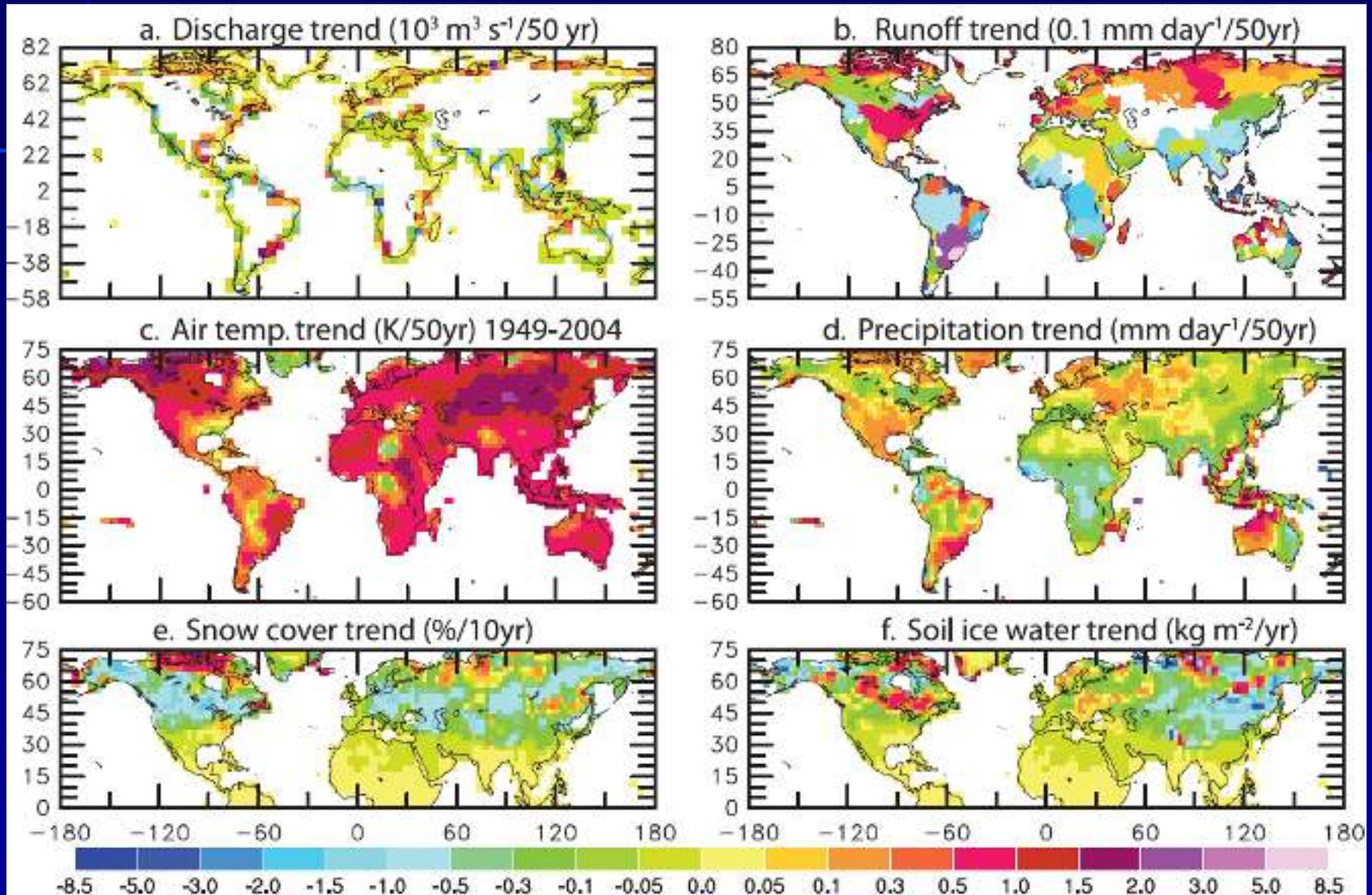
Major effects of anthropogenic vectors

- (i) *Human activities largely accelerate biogeochemical cycles and the transfer of materials at the planetary levels;*
- (ii) *Natural fluvial filters have been constantly altered, particularly by the construction of dams and deforestation of gallery forests and conversion of coastal vegetation;*
- (iii) *Fluvial discharges to the oceans are presently artificially controlled and reduced by engineering interventions (dams, diversion withdraw) and due to global climate change, at least in lower latitudes).*

Principals classes of anthropogenic vectors affecting the transport of materials at the continent-ocean interface

Vectors	Pressure	Impact
Agribusiness/ Aquaculture	Increasing loads of sediments, nutrients and contaminants, permeability of surfaces, decreasing water availability	Sedimentation Eutrophication
Urbanization / Industrialization		Sedimentation Eutrophication Contamination
Dams	Retention of sediments and nutrients Regularization of the fluvial flux	Sedimentation Erosion Oligotrophy
Global climate change	Sea level rise, alteration of the rainfall regime	Sedimentation Erosion

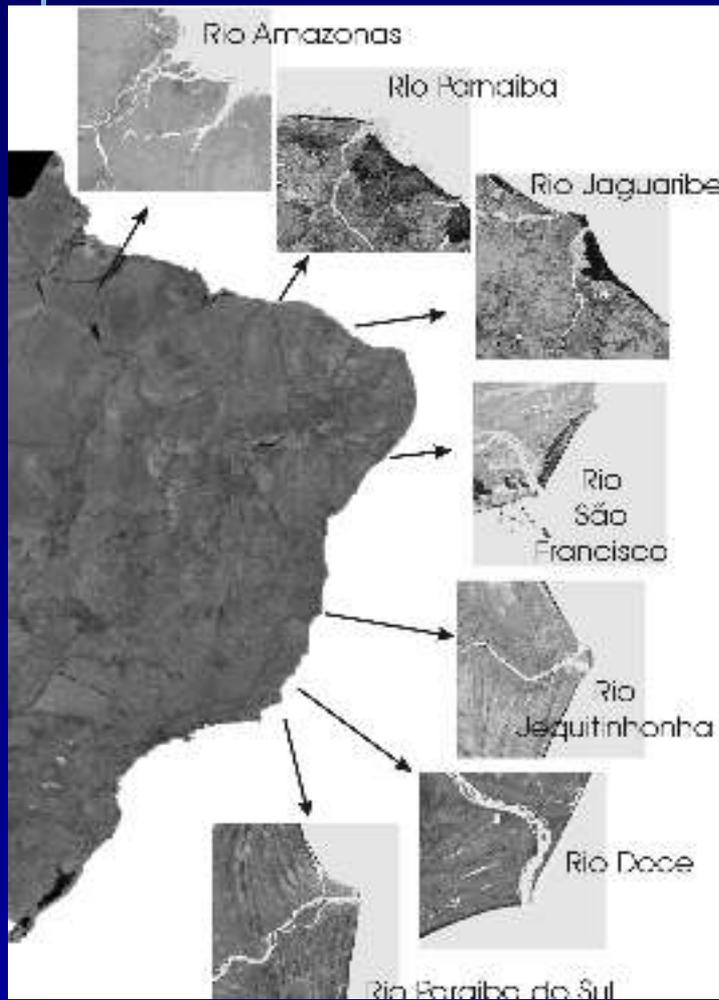
Global changes augment continental runoff in high latitudes, and decrease in lower latitudes and in semiarid regions in particular (Dai et al., 2009).



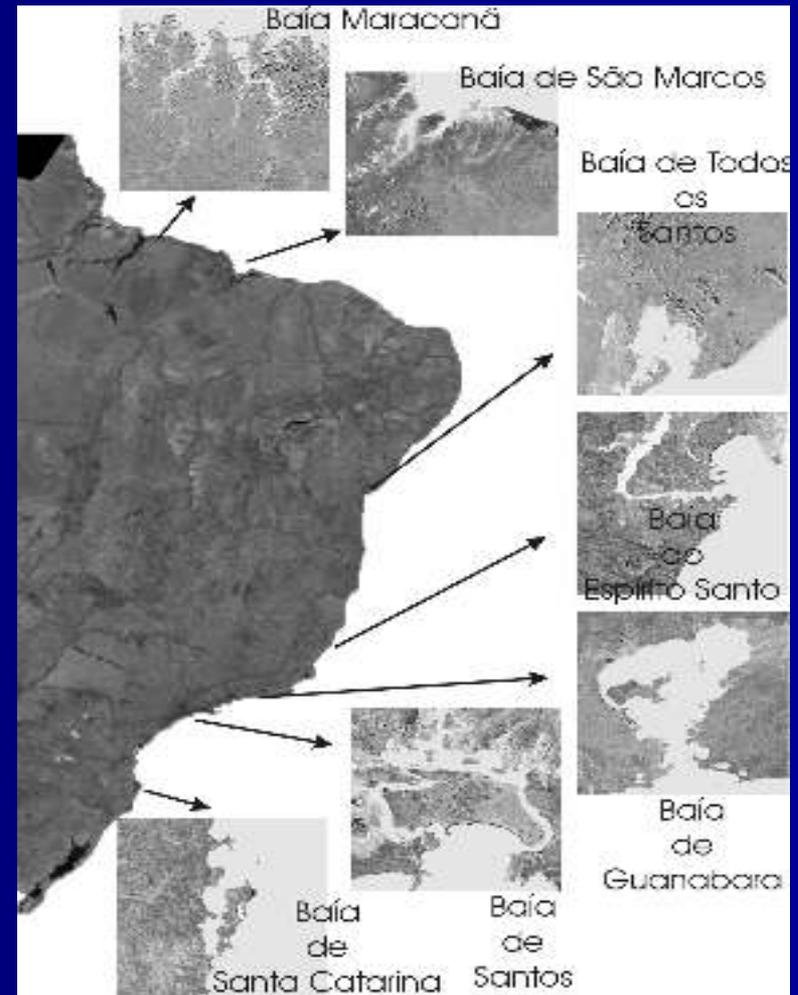
Classes of interface systems in Brazil (Knoppers *et al.*, 2009).

1. Spatial Scale

Exporters / Accumulators



Accumulators/ Exporters



Typical exporting systems form fluvial plumes over continental shelves, but may display seasonality



Descarga de sedimentos pelo Rio Jaguaribe, CE em 2004



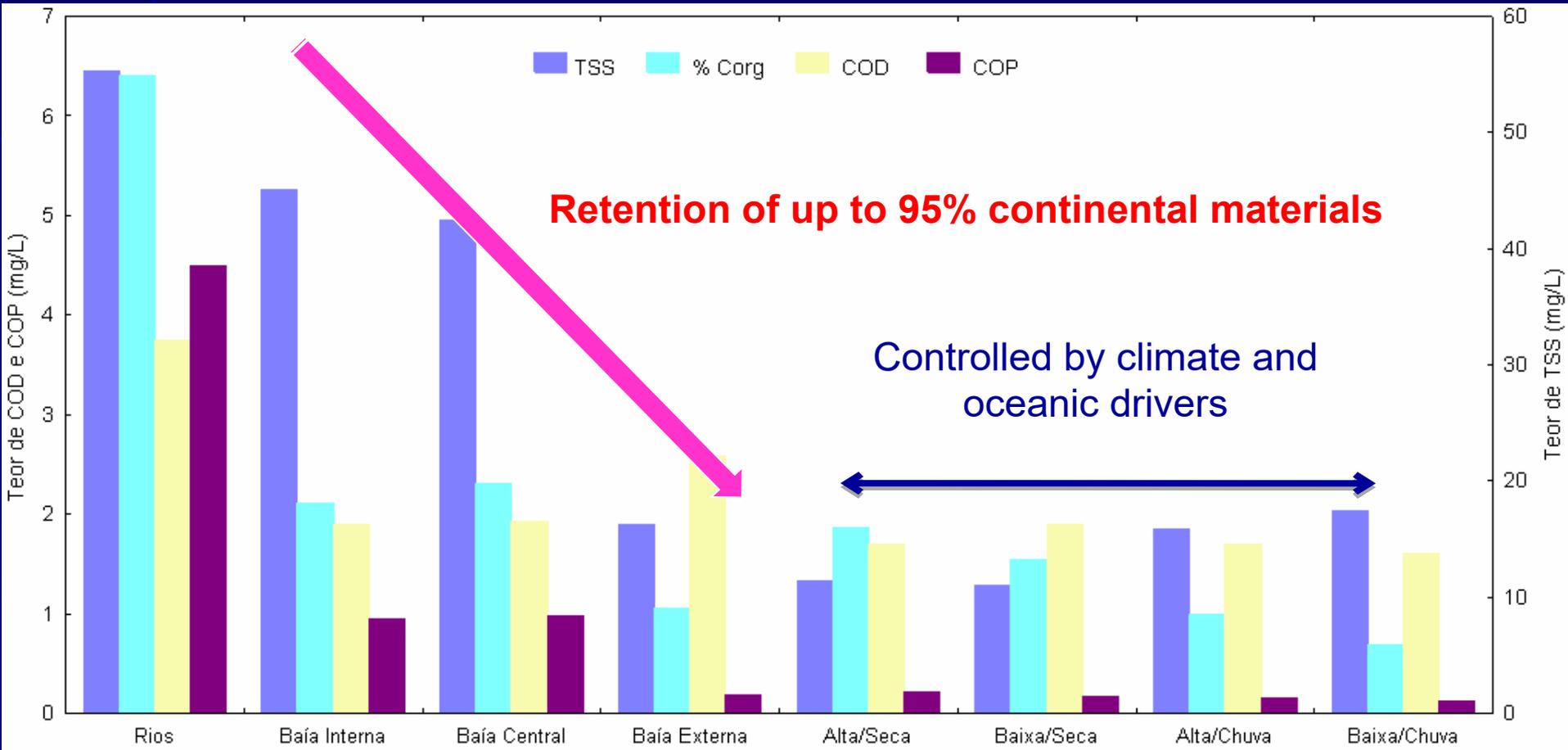
1. Spatial scale

Typical retainer systems forms
sedimentary environments in the estuarine
zone

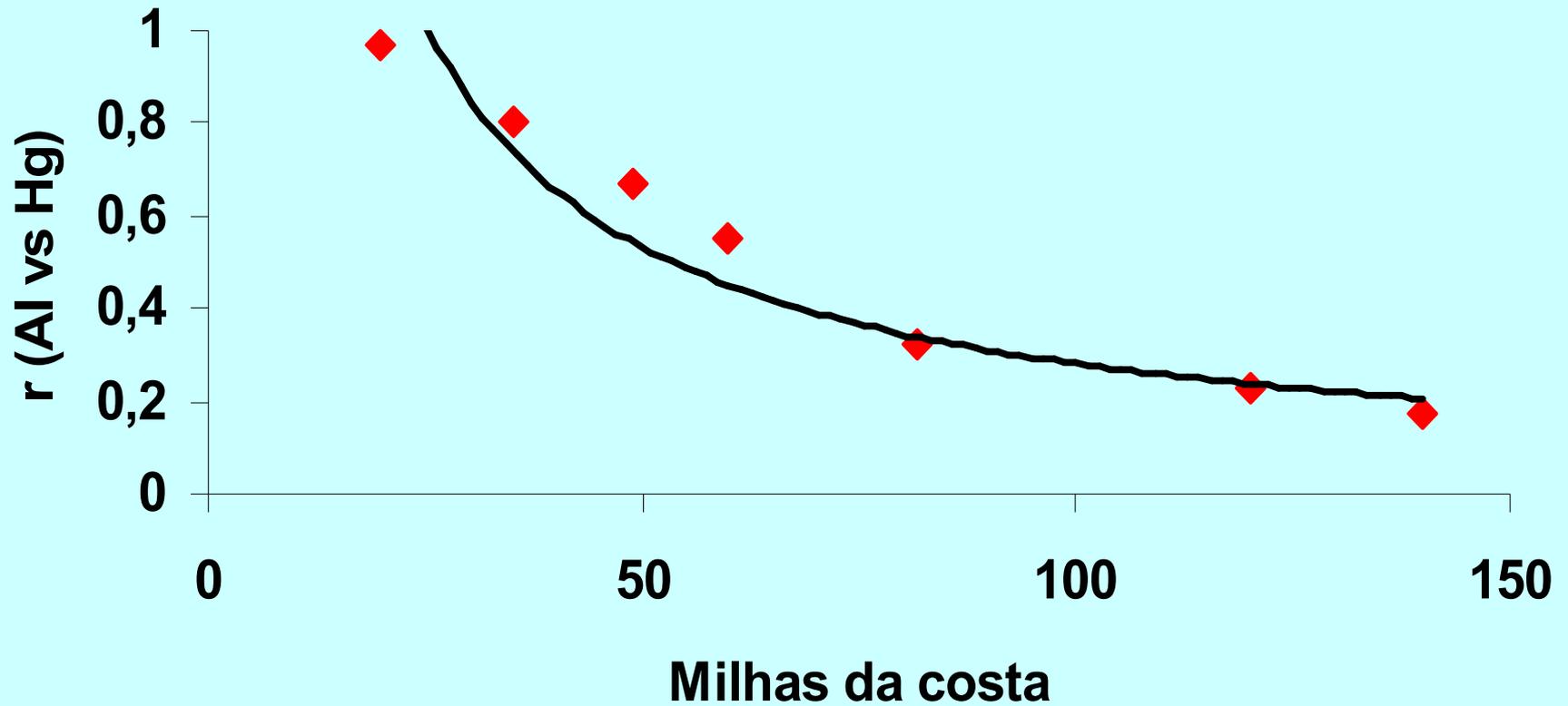
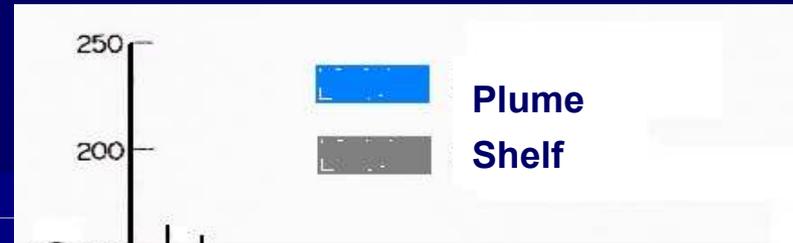


1. Spatial scale

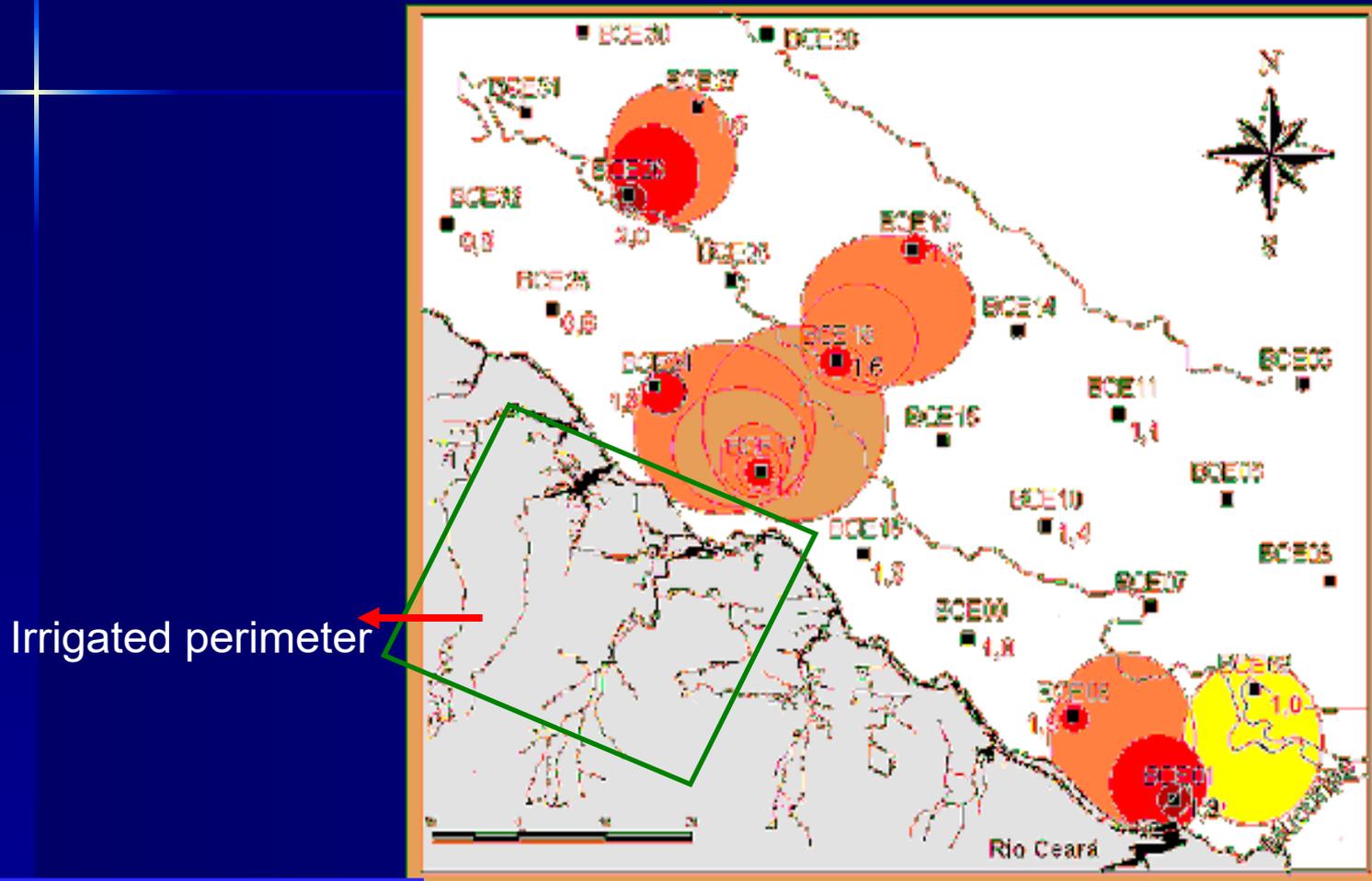
Concentration changes of COD, COP e TSS along Sepetiba Bay, SE Brazil



Hg vs Al in sediments along the continental shelf in SE Brazil

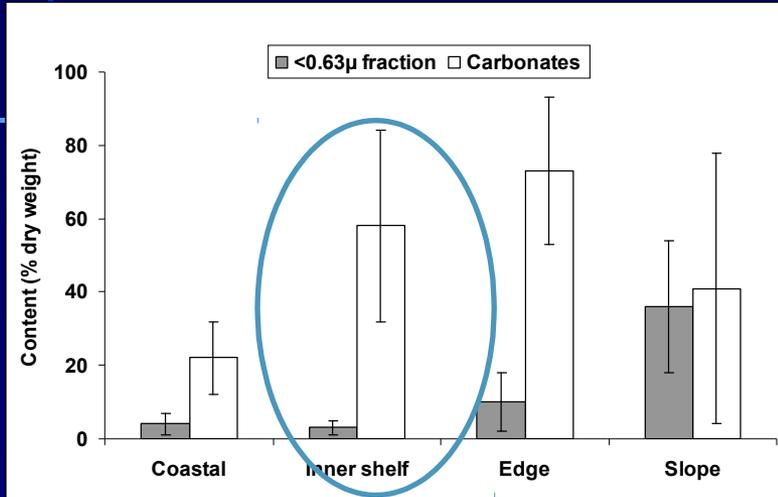


Al distribution in shelf sediments from NE Brazil

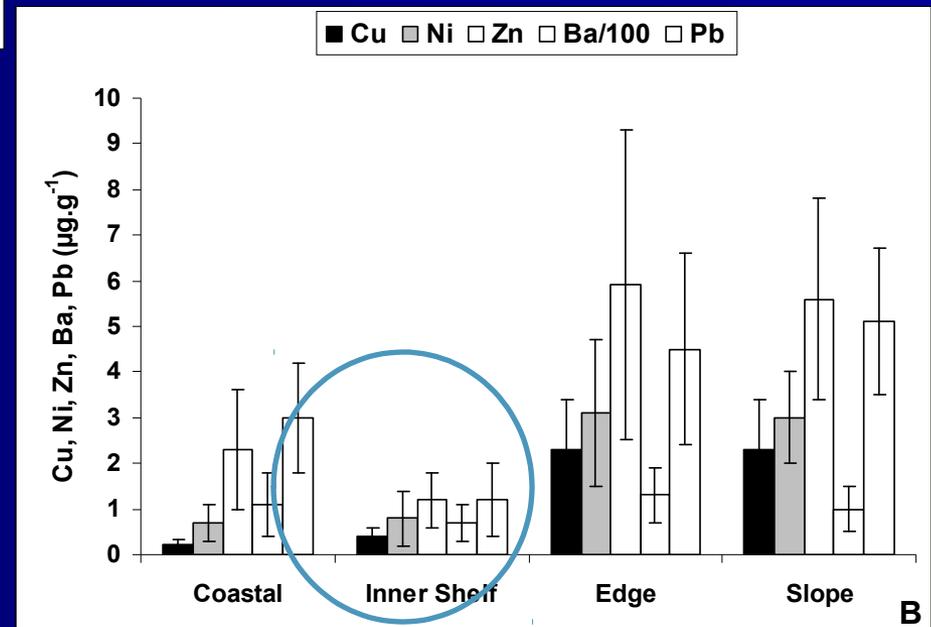


1. Spatial scale

Trace metals in shelf sediments in an offshore oil and gas exploration area in NE Brazil (Lacerda et al., 2013)



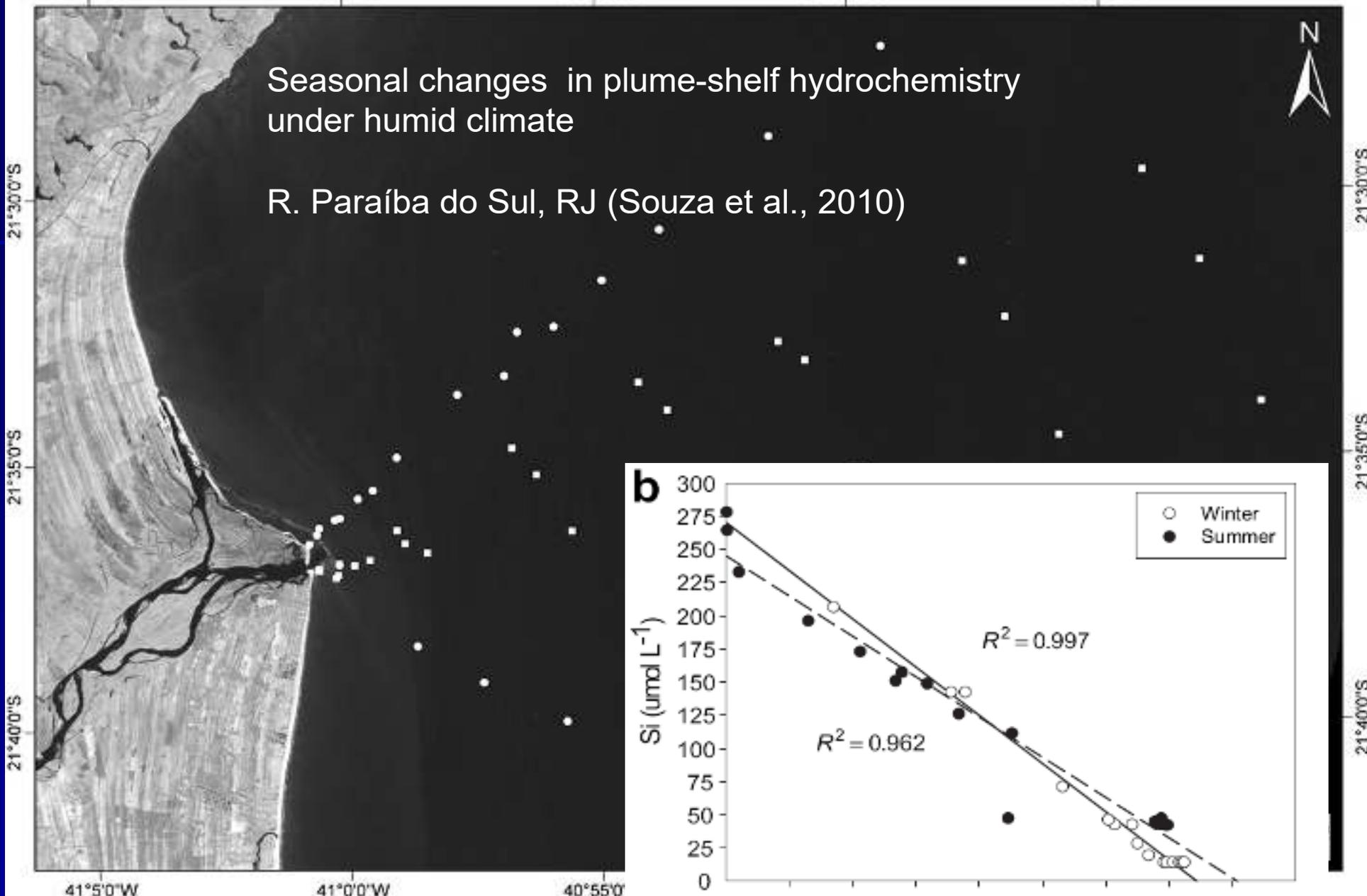
Potiguar Basin, RN



1. Spatial scale

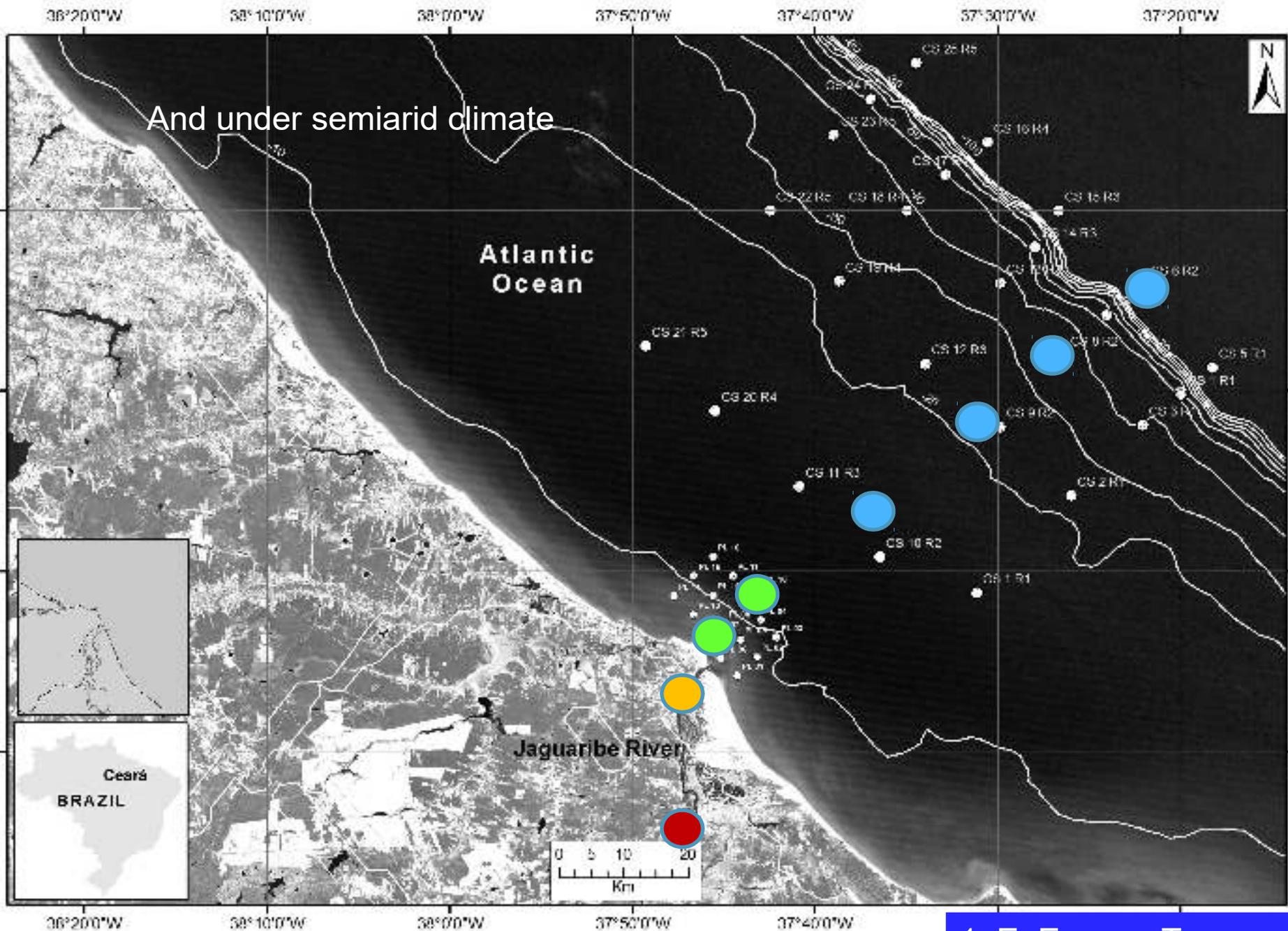
Seasonal changes in plume-shelf hydrochemistry under humid climate

R. Paraíba do Sul, RJ (Souza et al., 2010)



1. Space-temporal scale

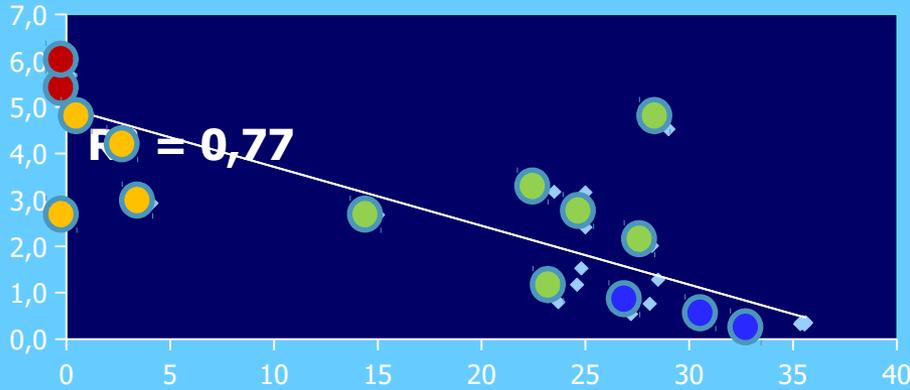
And under semiarid climate



Seasonality under semiarid climate

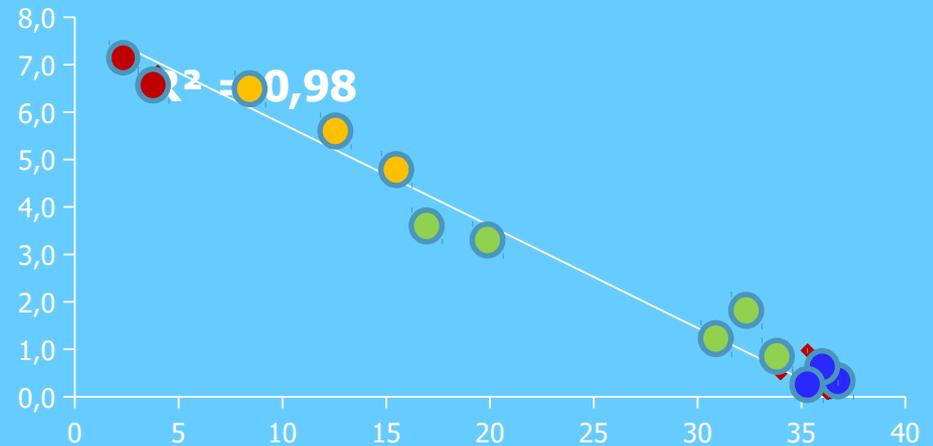
R. Jaguaribe, CE (Lacerda et al., 2010)

Si vs Salinidade, Período Chuvoso



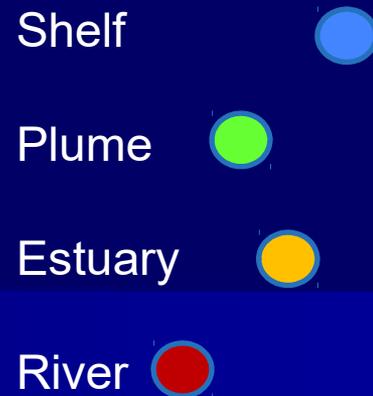
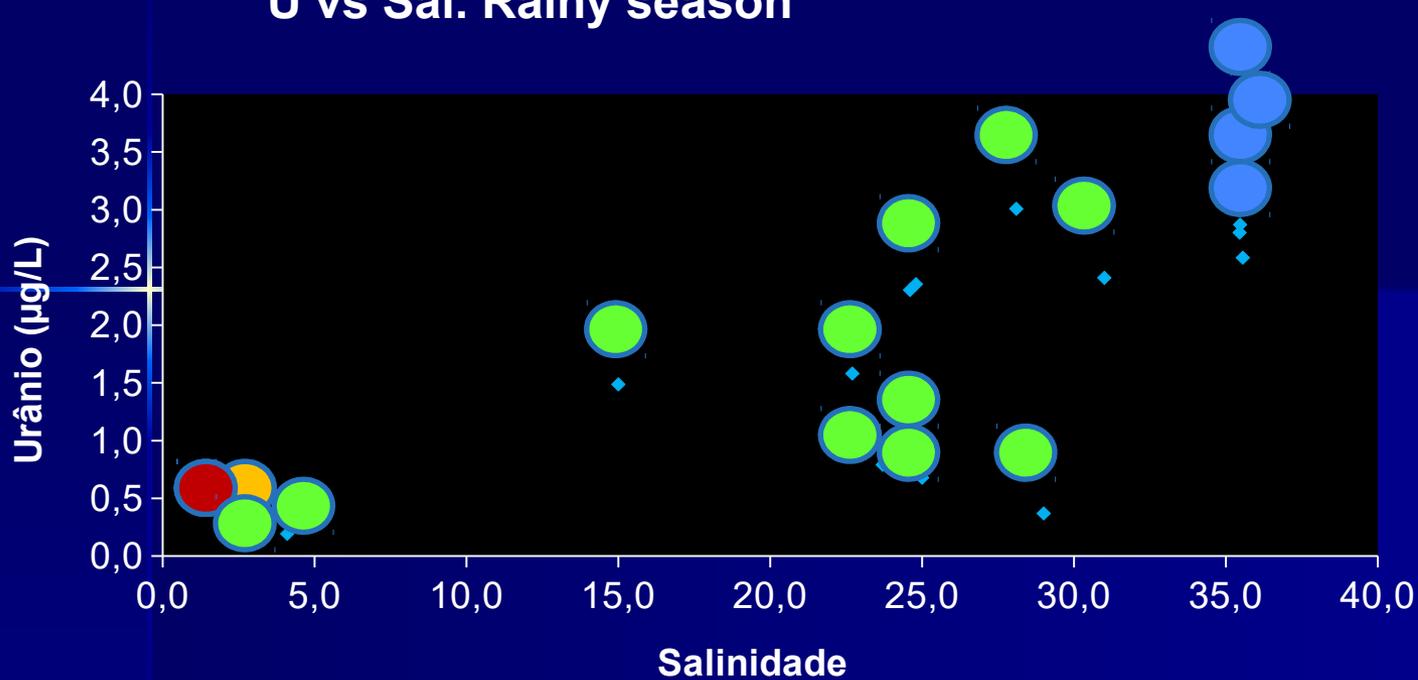
- Shelf 
- Plume 
- Estuary 
- River 

Si vs Salinidade, Estação Seca

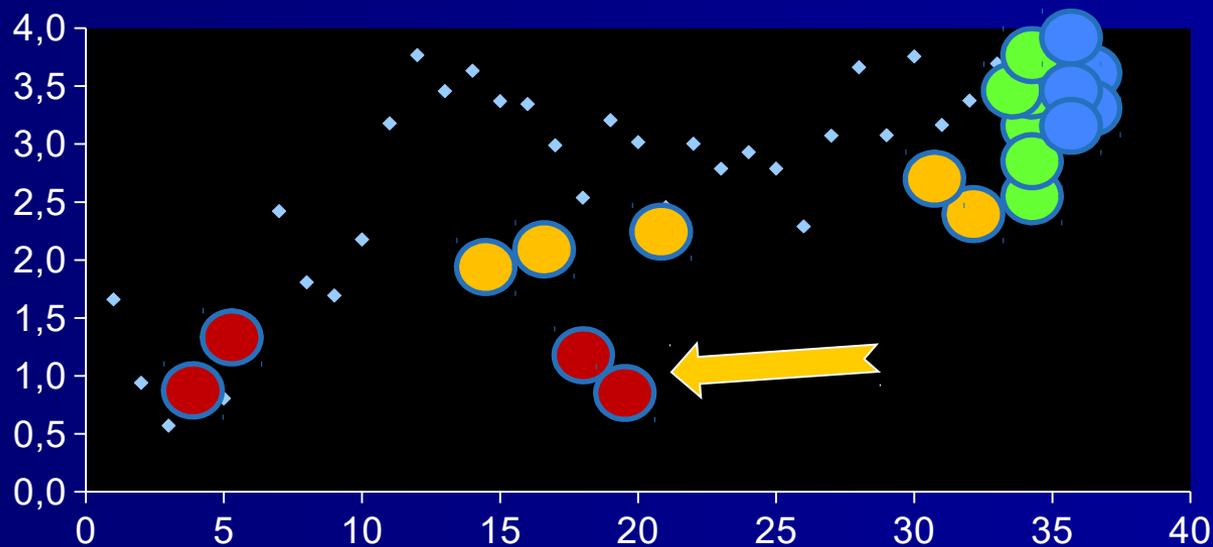


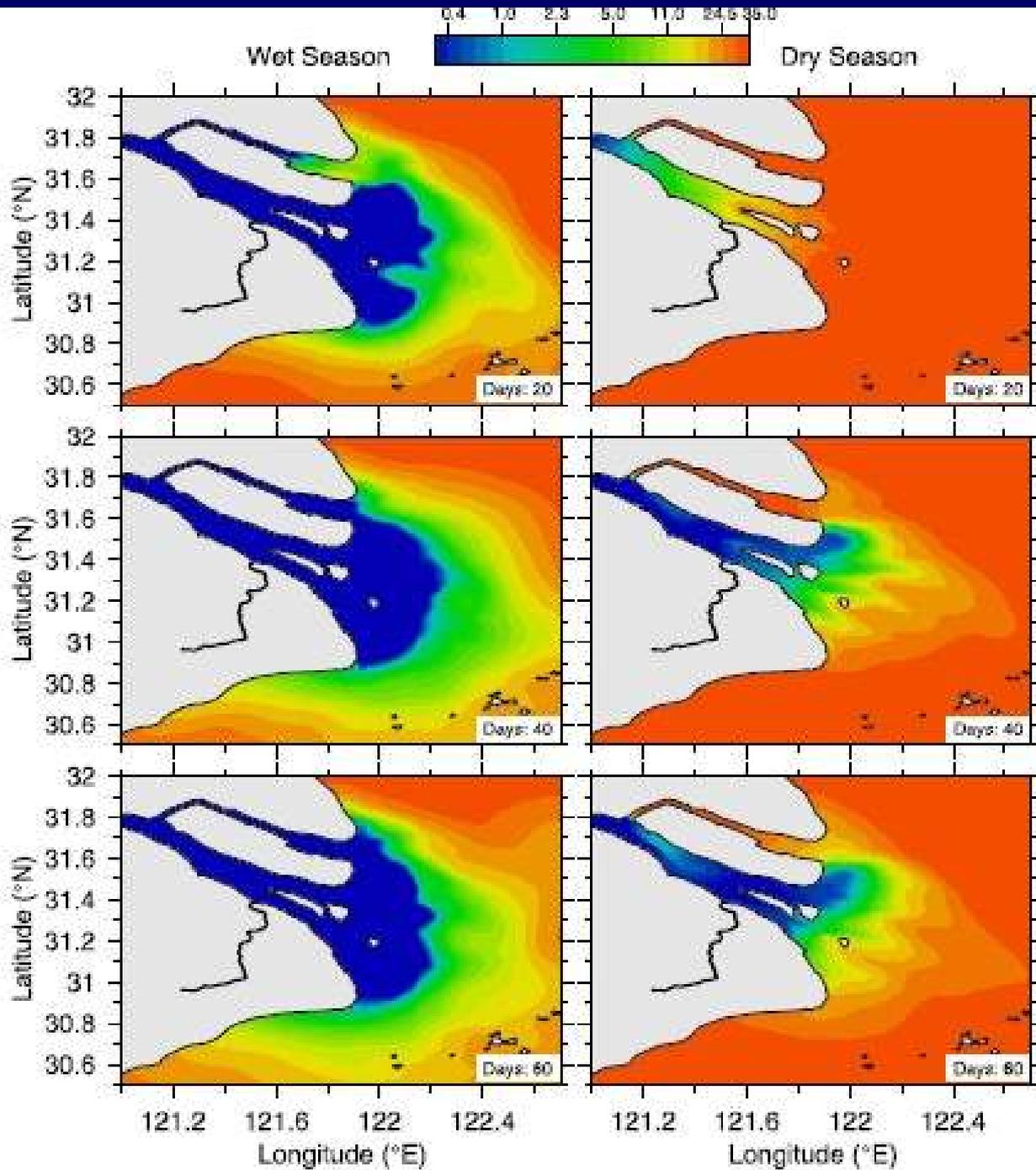
1. Space-temporal scale

U vs Sal. Rainy season



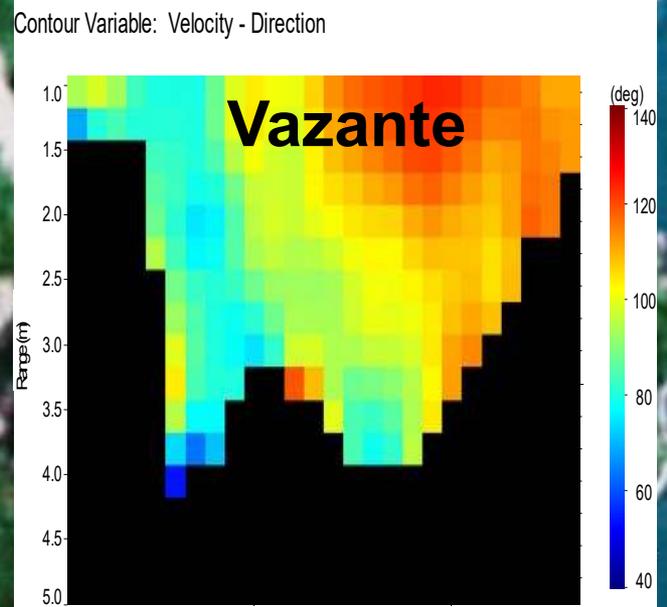
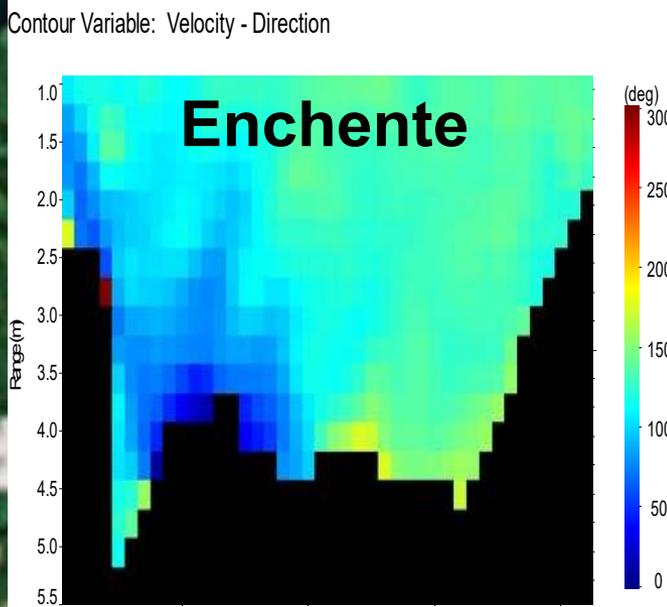
U vs Sal. Dry season





Salt intrusion at
the Yangtze,
China
*c.f. LOICZ
(2010)*

Fluxes (ADCP) under umid climate
Rio de Contas, Itacaré, BA

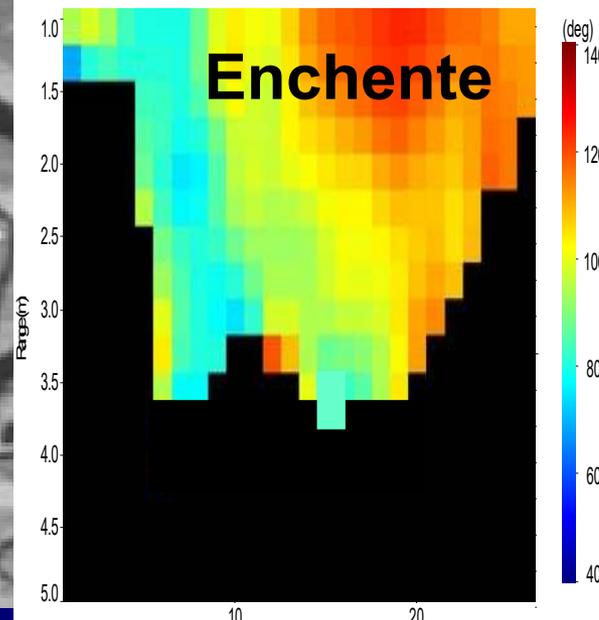


2. Space-temporal scale

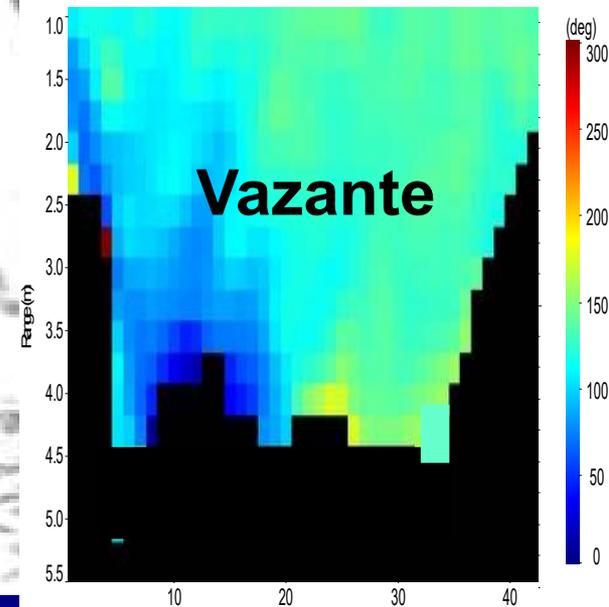
**Fluxes under
semiarid climate
(ADCP)**

**Rio Jaguaribe,
Fortim, CE**

Contour Variable: Velocity - Direction



Contour Variable: Velocity - Direction



Globally, about 40% of transported materials from continental origin by rivers are trapped in estuarine and deltaic sediments.

Materials passing through the estuarine-deltaic filter are deposited in the continental shelf according to shelf characteristics.

Less than 10% is eventually exported to the deep ocean

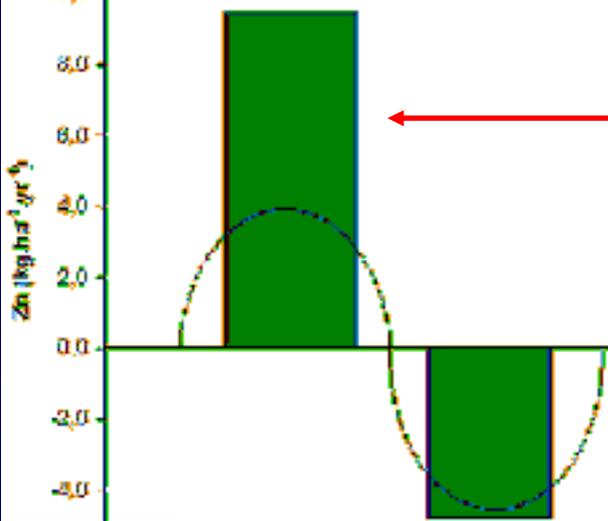


Post-depositional colonization of estuarine and deltaic sediments by plants changes the biogeochemical nature of the environment



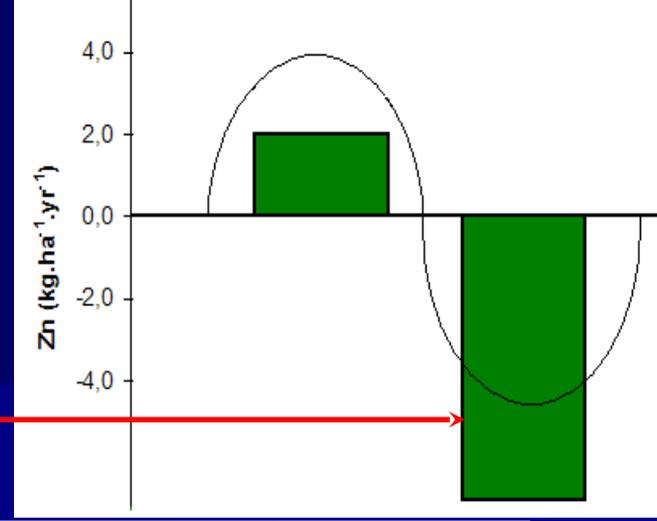
e.g. Impact from mangrove colonization of
significance to estuarine ecology and sustainable use

- Augment of the deposition of fine sediments and sedimentation rates
- Decreasing aeration of sediments
- Increasing organic matter deposition and preservation in sediments
- Increasing consumption of dissolved oxygen
- Anoxia & sulfate reduction



Accumulation of Zn in neap tides

Export of Zn in spring tides



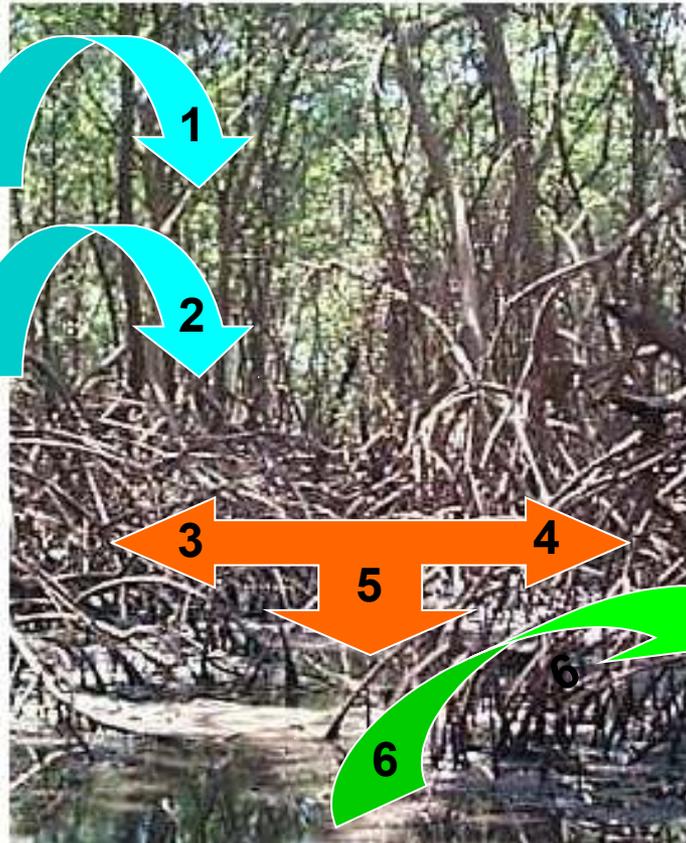
Lacerda (1998)

Tidal deposition of metals associated with oxidized organic matter

Trapping of TSS by roots
Deposition under anoxic conditions

Oxides dissolution

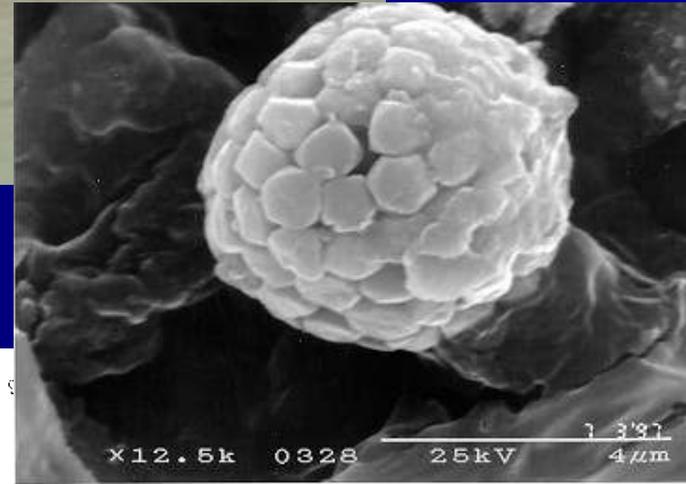
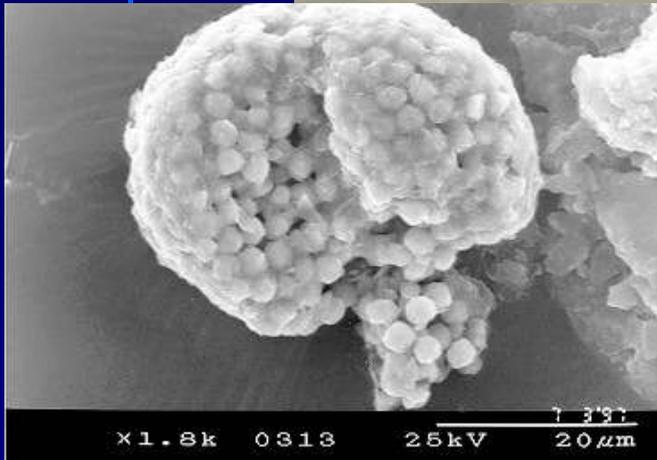
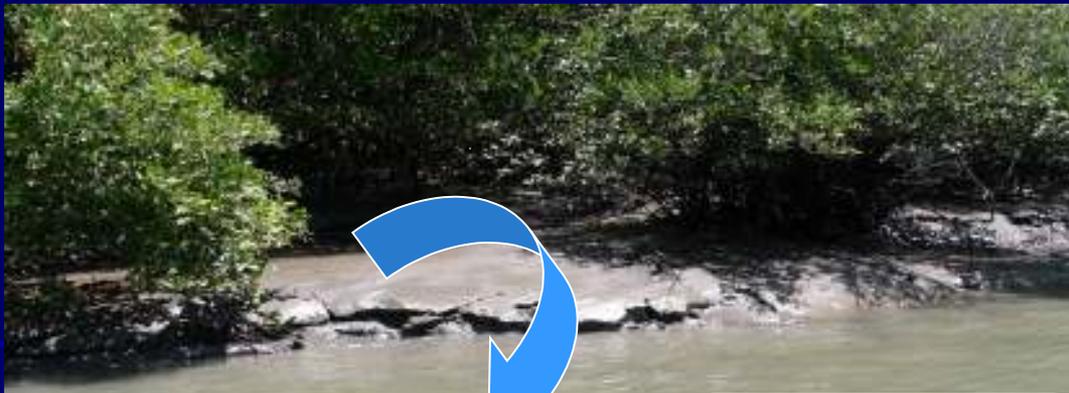
Sulfide formation by incomplete anaerobic decomposition of organic matter by sulfate reducing bacteria



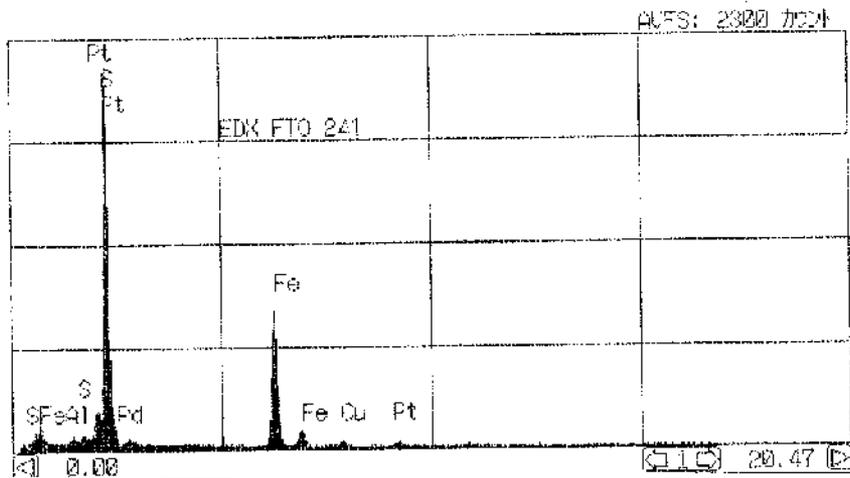
Food web transfer

Export of organic-metal complexes

Sulfide precipitation and metal burial in sediments



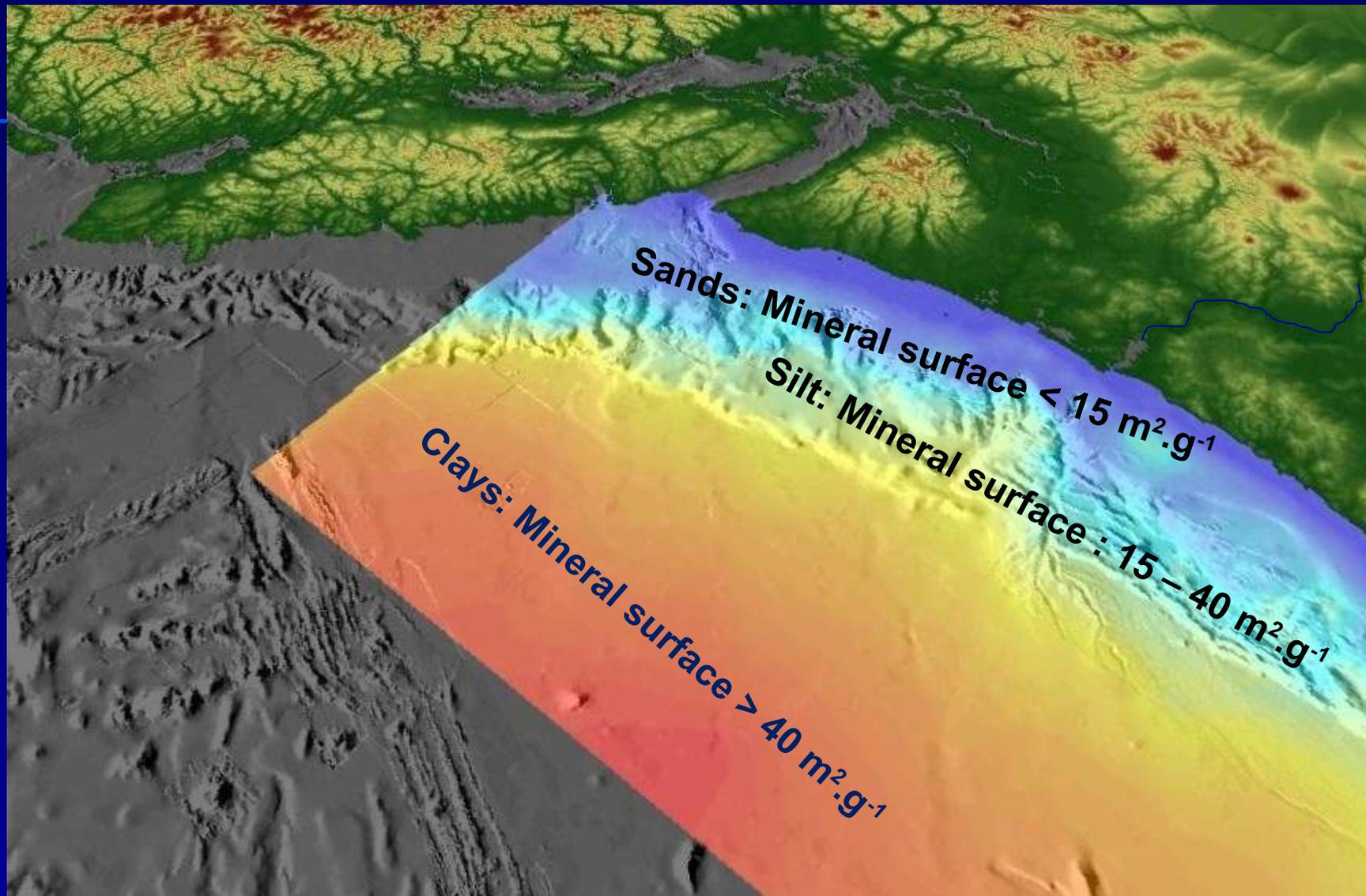
測定時間: 100 s

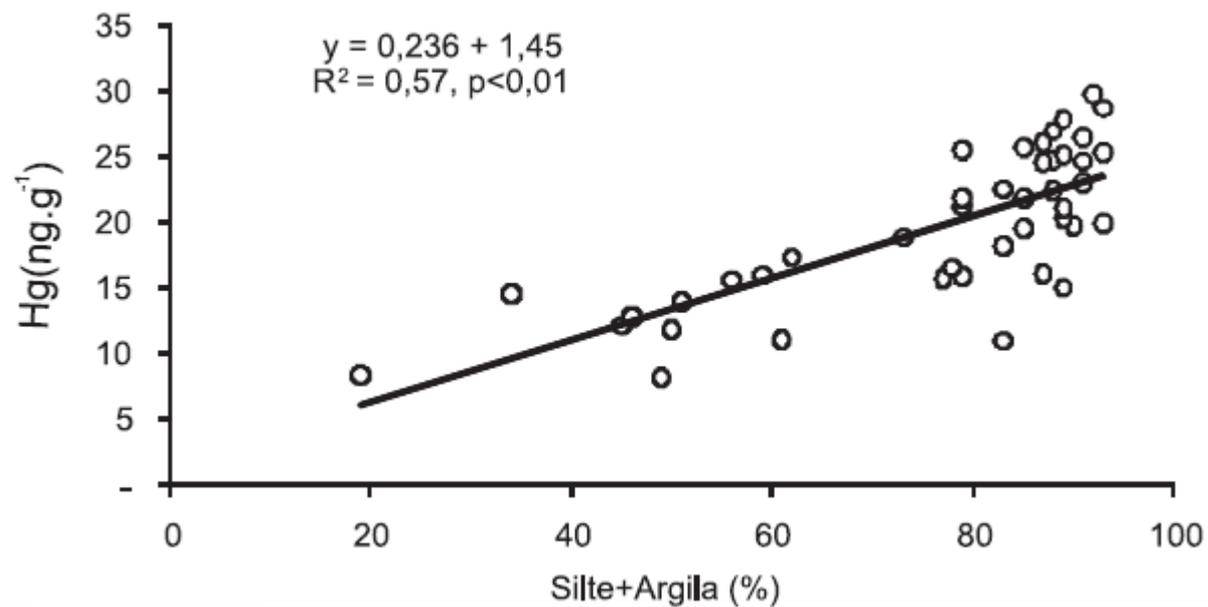
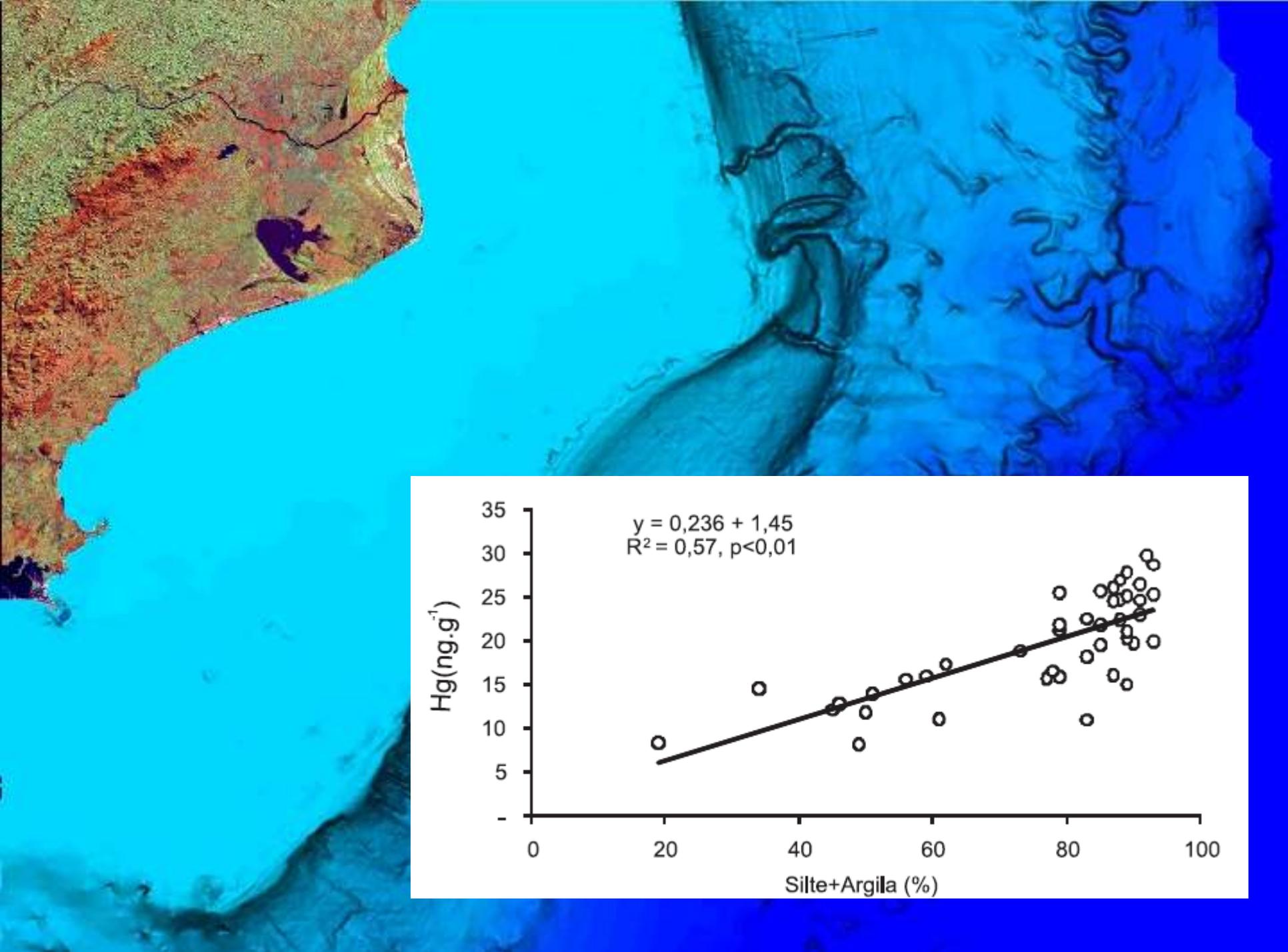


Framboids of pyrites that release metals upon oxidation due to erosion and sea level rise or decreasing fluvial sediment transport

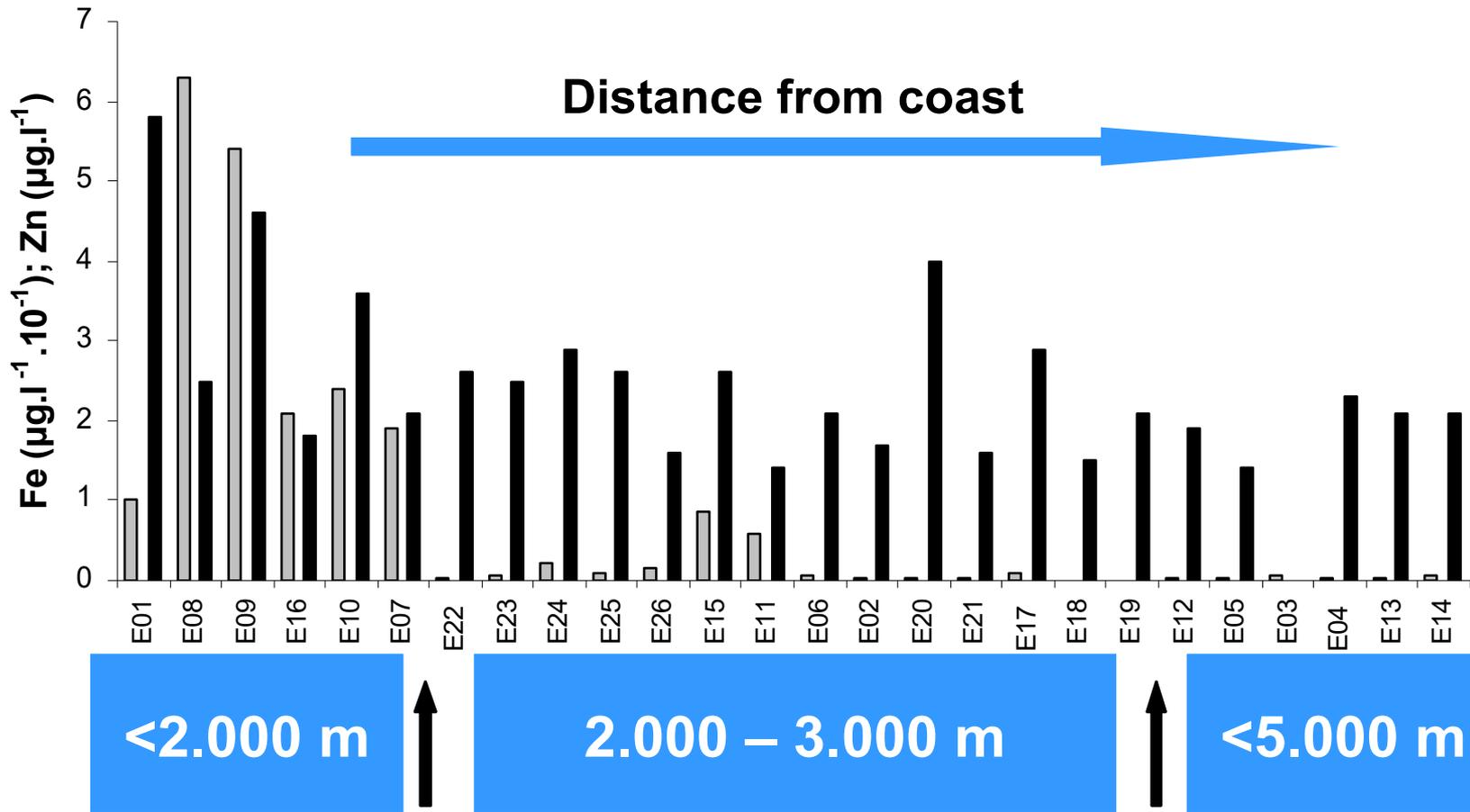
Pires & Lacerda (2007)

Typical granulometry of shelf sediments



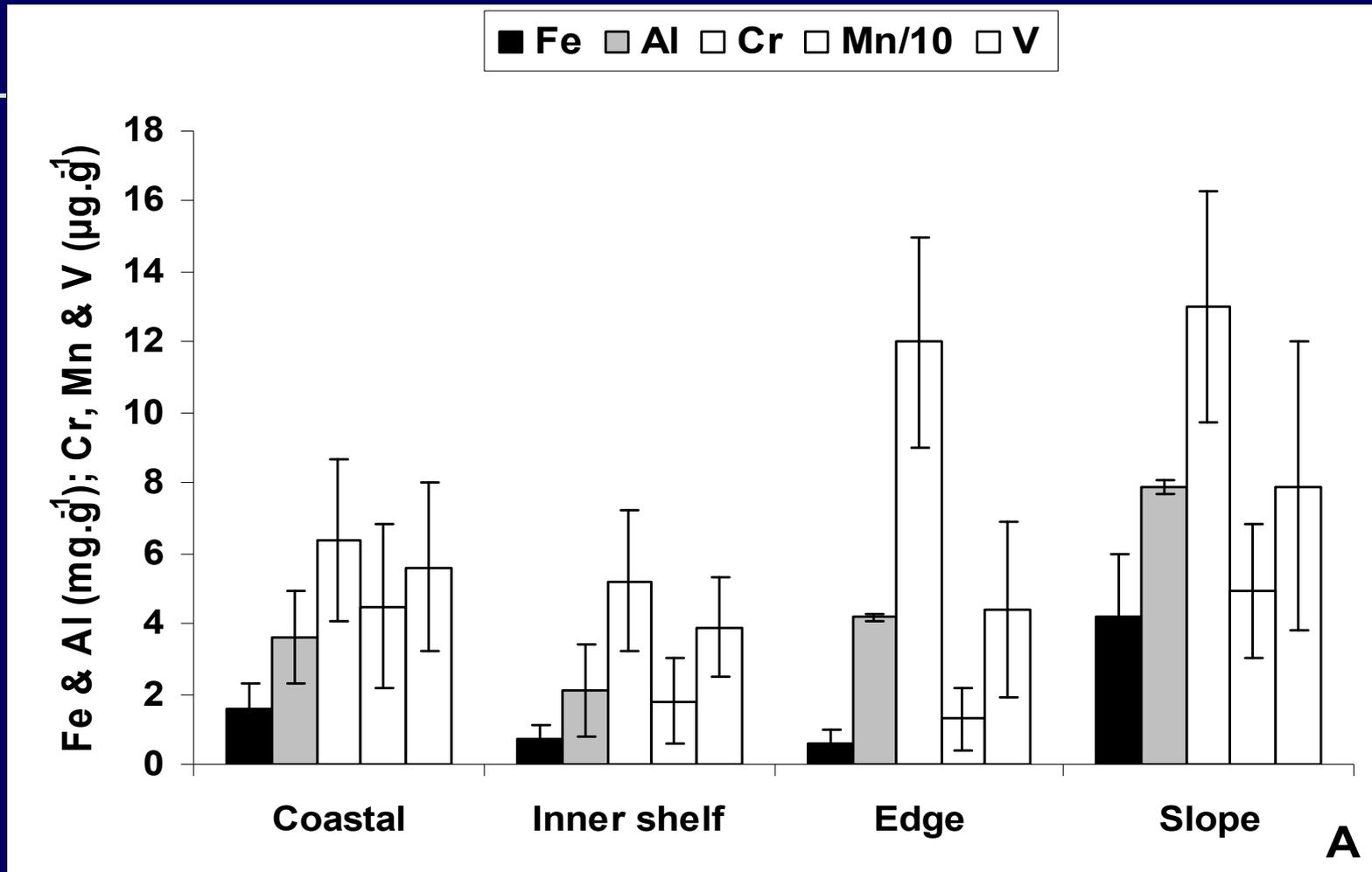


Metal distribution in NE Brazil shelf sediments



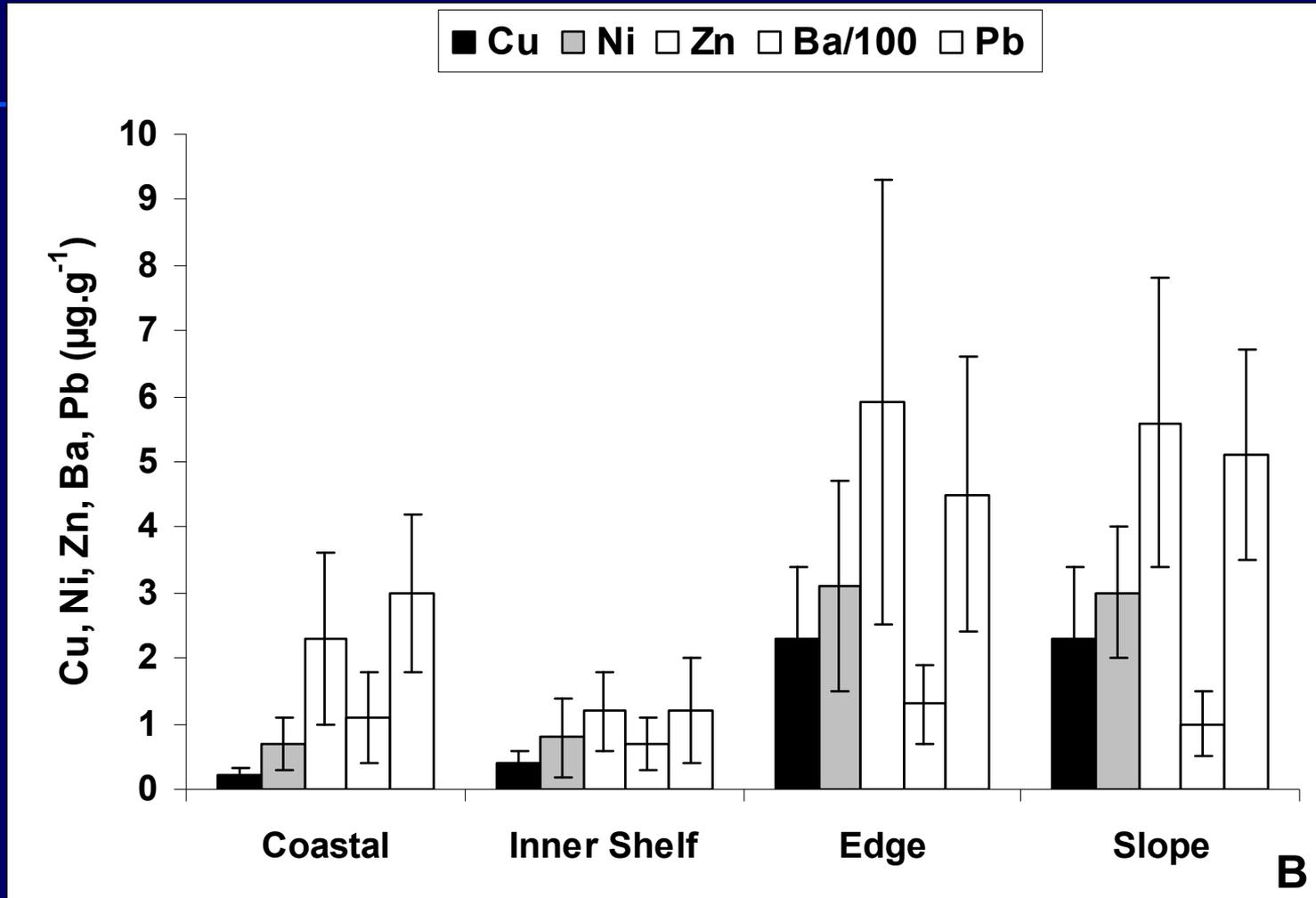
Influence of continental sources

Metal distribution in NE Brazil shelf sediments



Influenced by marine processes

Metal distribution in NE Brazil shelf sediments



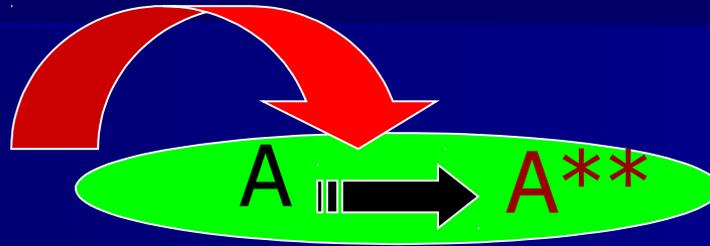
Influenced by marine processes

“The magnitude of transfer processes are today controlled mostly by anthropogenic drives”.

Forms of action

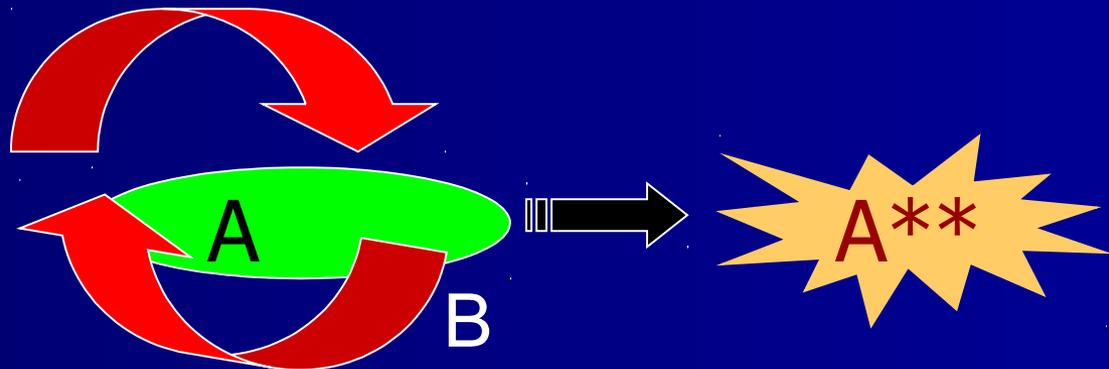
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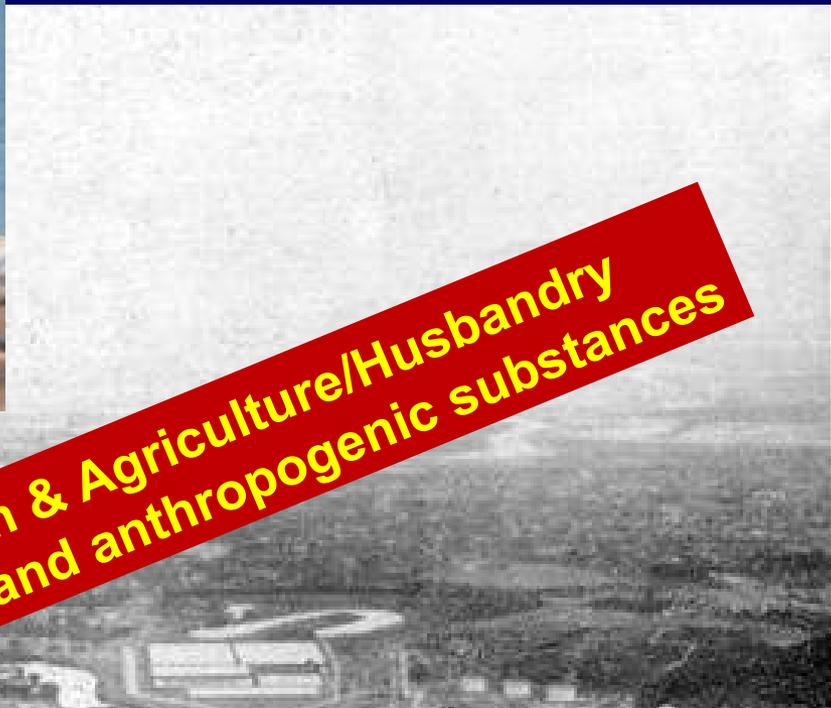
Vectors causing direct changes on the biogeochemical properties of the environment through emission of alien substances (mostly typical of the last century)



2

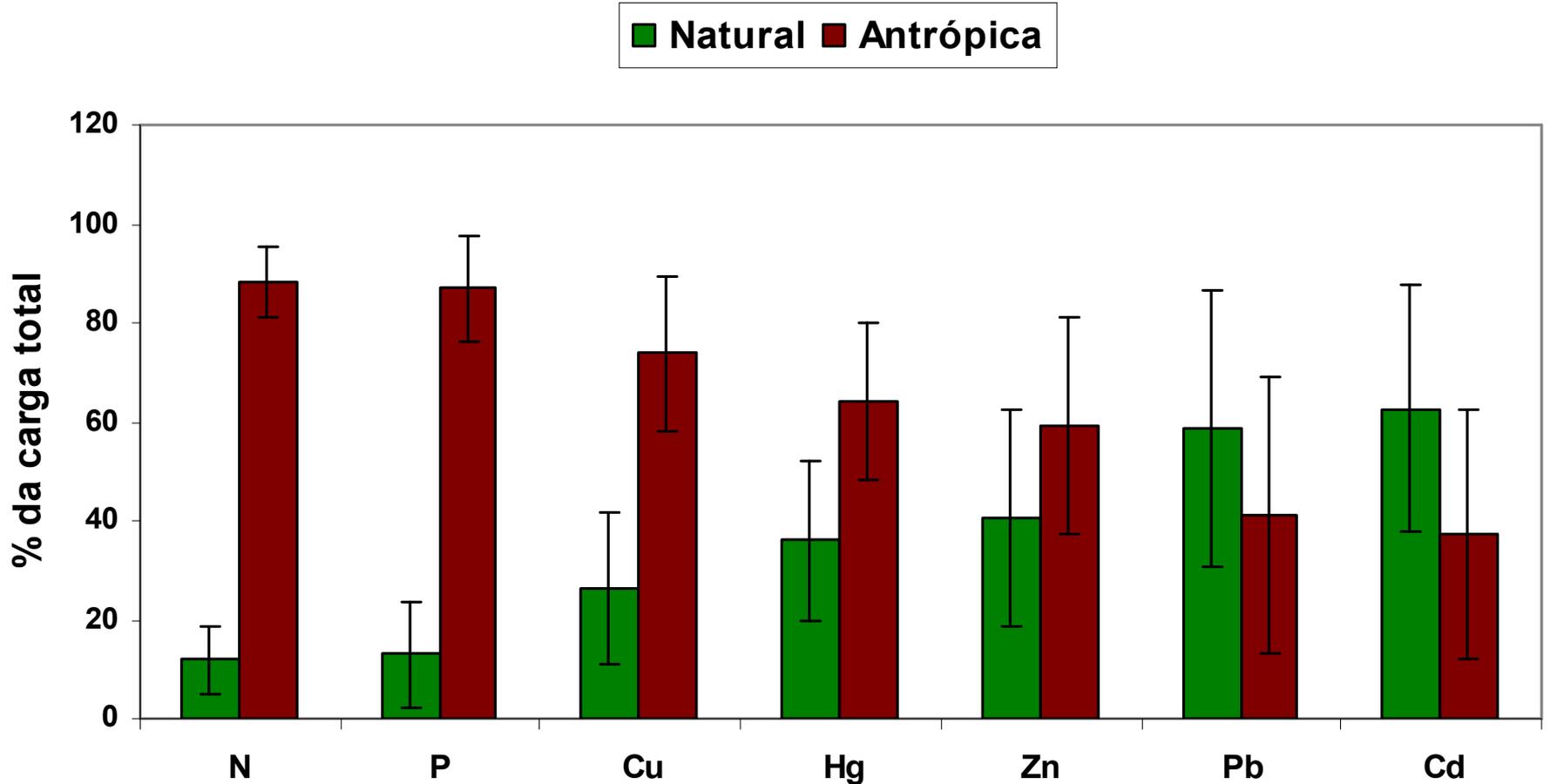
Vectors causing direct changes on the biogeochemical properties of the environment through interactions with its properties or among themselves (our challenger today).





**Urbanization & Industrialization & Agriculture/Husbandry
Increasing discharges of natural and anthropogenic substances**

Relative importance of natural and anthropogenic sources of nutrients and metals to the NE Coast of Brazil. Average values from 19 estuaries.



Sources	Emission factors N and P (t/km ² /year); Cu, Hg and Zn (kg/km ² /year)		Substances present in effluent		
Natural sources	N = 0.05 – 0.9 P = 0.01 – 0.06	Cu = 2.0 – 2.6 Zn = 5.0 – 6.5 Hg = <0.001	Mostly associated with particulate matter		Receiving body
Agriculture	N = 0.05 – 2.65 P = 0.12 – 0.56	Cu = 0.7 – 13.5 Zn = 0.04 – 0.13 Hg = 0.02	Nitrate; Ammonia; Phosphate	Cu ²⁺ , Zn ²⁺ , Particulate- Cu and Zn	Soil
Husbandry	N = 0.09 – 1.31 P = 0.09 – 1.73	Cu = 0.3 – 1.0 Zn = 0.4 – 7.3 Hg = <0.001	Ammonia; Phosphate	Particulate- Cu and Zn	Soil
Urban waste waters and runoff	N = 0.03 – 0.55 P = 0.01 – 0.14	Cu = 0.1 – 15.3 Zn = 0.01 – 47.2 Hg = < 0.001	Nitrate; Ammonia; Phosphate; Particulate-P	Cu ²⁺ , Zn ²⁺ , Hg ²⁺ ; Particulate- Cu and Zn	Soil, waterways and estuaries
Urban solid wastes disposal	N = 0.001 – 0.2 P < 0.0001	Cu = 0,001 – 0,03 Zn = 0,001 – 0,07 Hg = 0.04	Dominant forms of N and P are too site-specific	Cu ²⁺ , Zn ²⁺ , Hg ²⁺ ; Particulate- Cu and Zn	Soil
Shrimp aquaculture	N = 1.25 – 4.09, P = 0.13 – 0.32	Cu = 38.6 – 59.8 Hg = 0.03 – 0.04 Zn = 508	PON (70%); NO ₃ ⁻ ; Ammonia; NO ₂ ⁻ ; POP; Phosphate	Particulate- Cu, Zn and Hg	Waterways and estuaries

Fortaleza, 1939



6,7 tPb.ano⁻¹
0,041 tHg.ano⁻¹
164 tN.ano⁻¹

Changes in soil uses

Urbanization

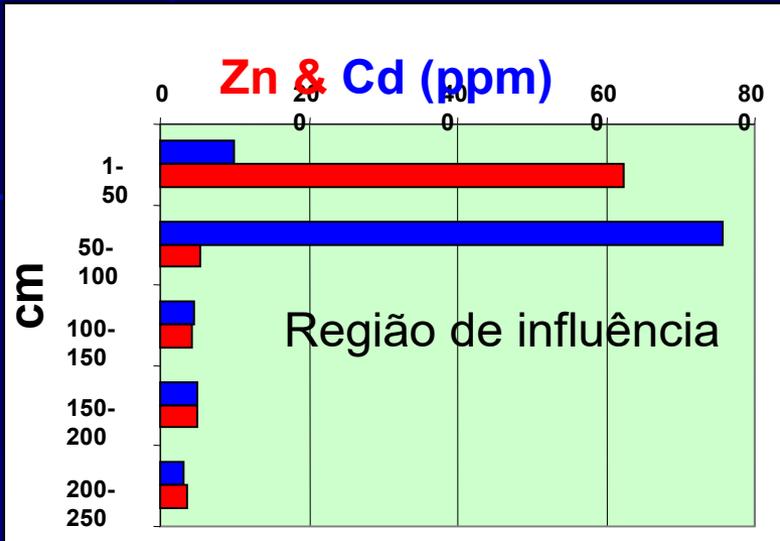
Fortaleza, 2007



117 tPb.ano⁻¹
0,578 tHg.ano⁻¹
7.200 tN.ano⁻¹

Legacy of irresponsible technologies faces lack of governance

Industrialization



Changes in soil use: **Agriculture**

Natural

0,45 tN.km⁻².ano⁻¹

0,03 tP.km⁻².ano⁻¹

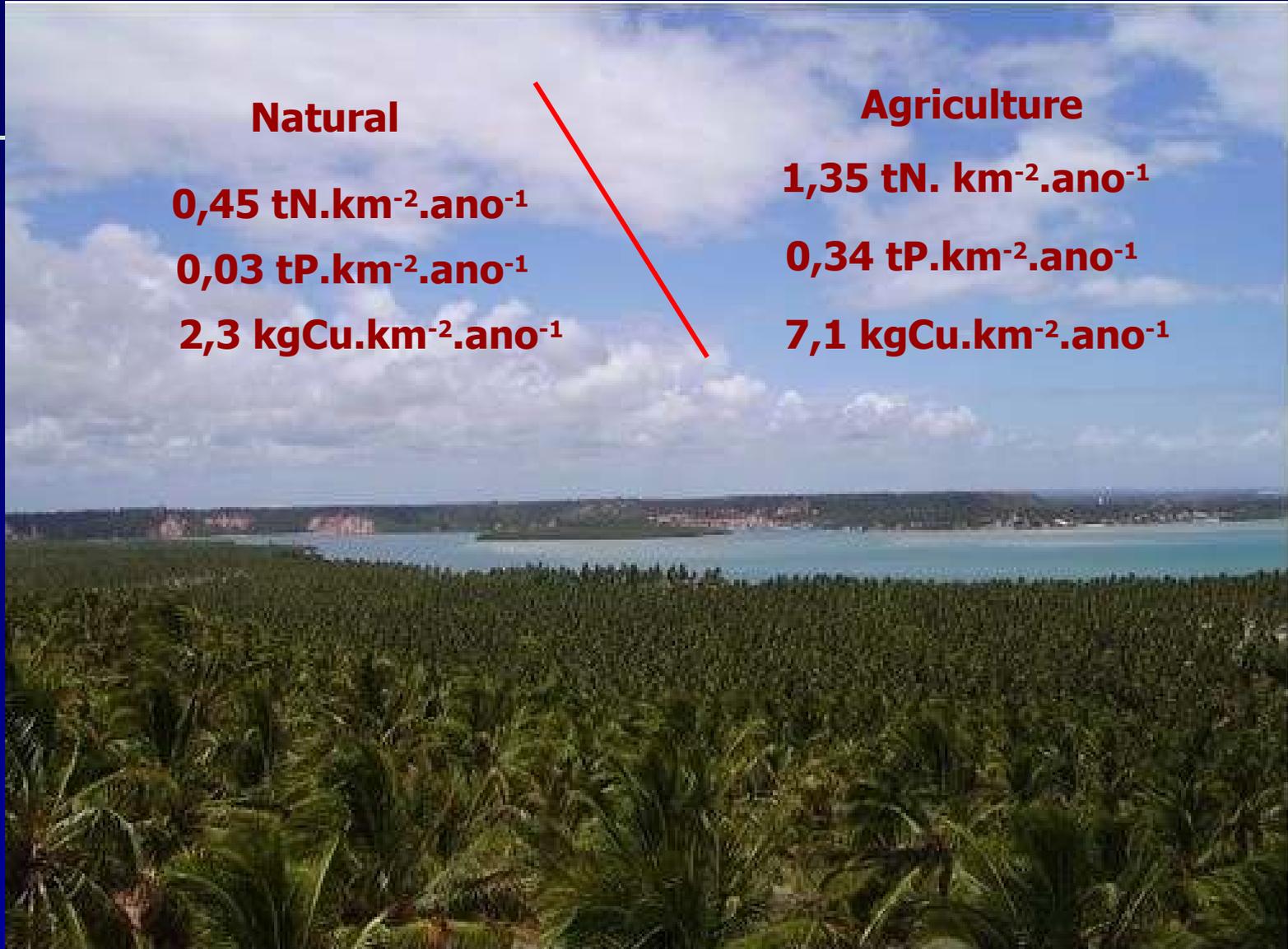
2,3 kgCu.km⁻².ano⁻¹

Agriculture

1,35 tN. km⁻².ano⁻¹

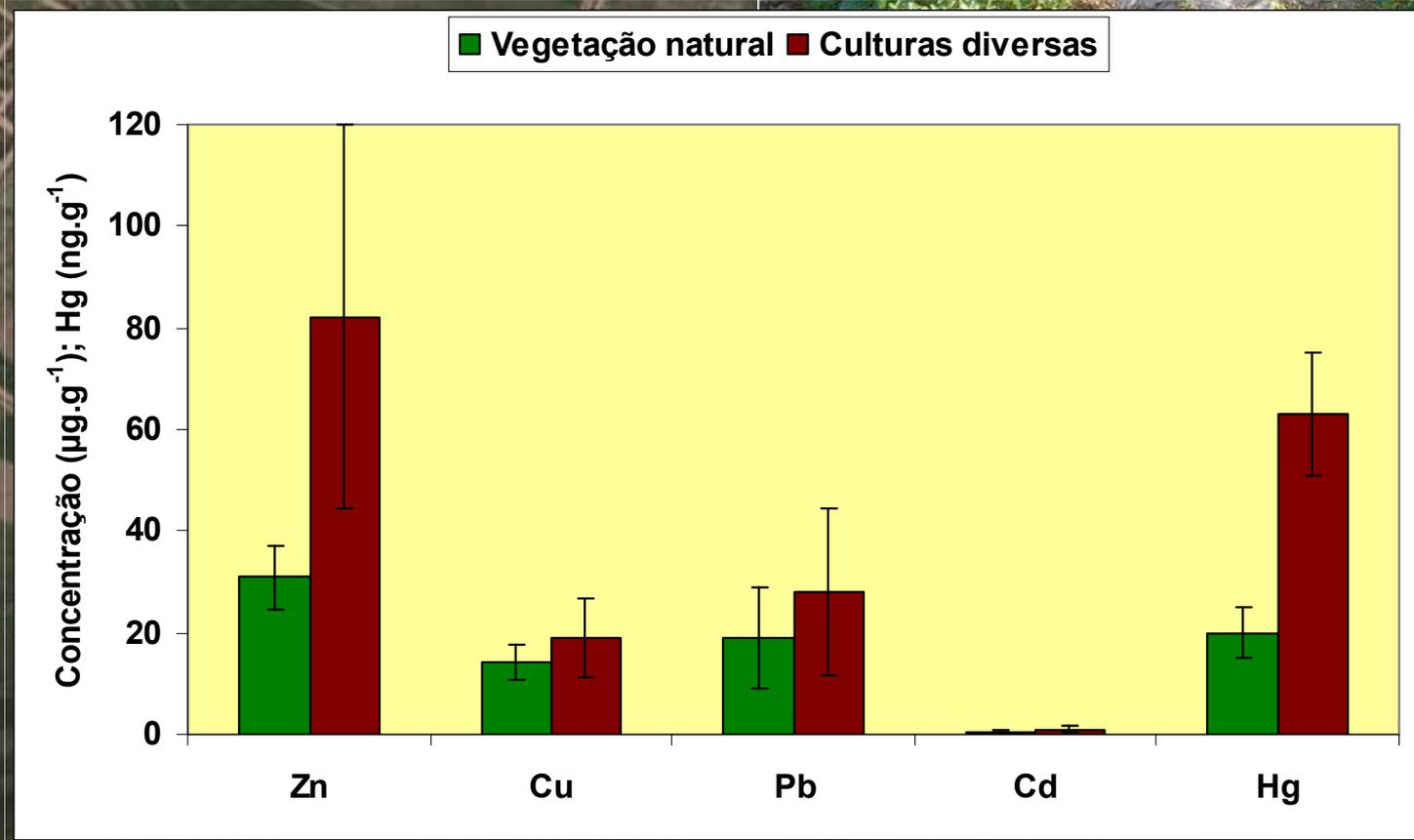
0,34 tP.km⁻².ano⁻¹

7,1 kgCu.km⁻².ano⁻¹

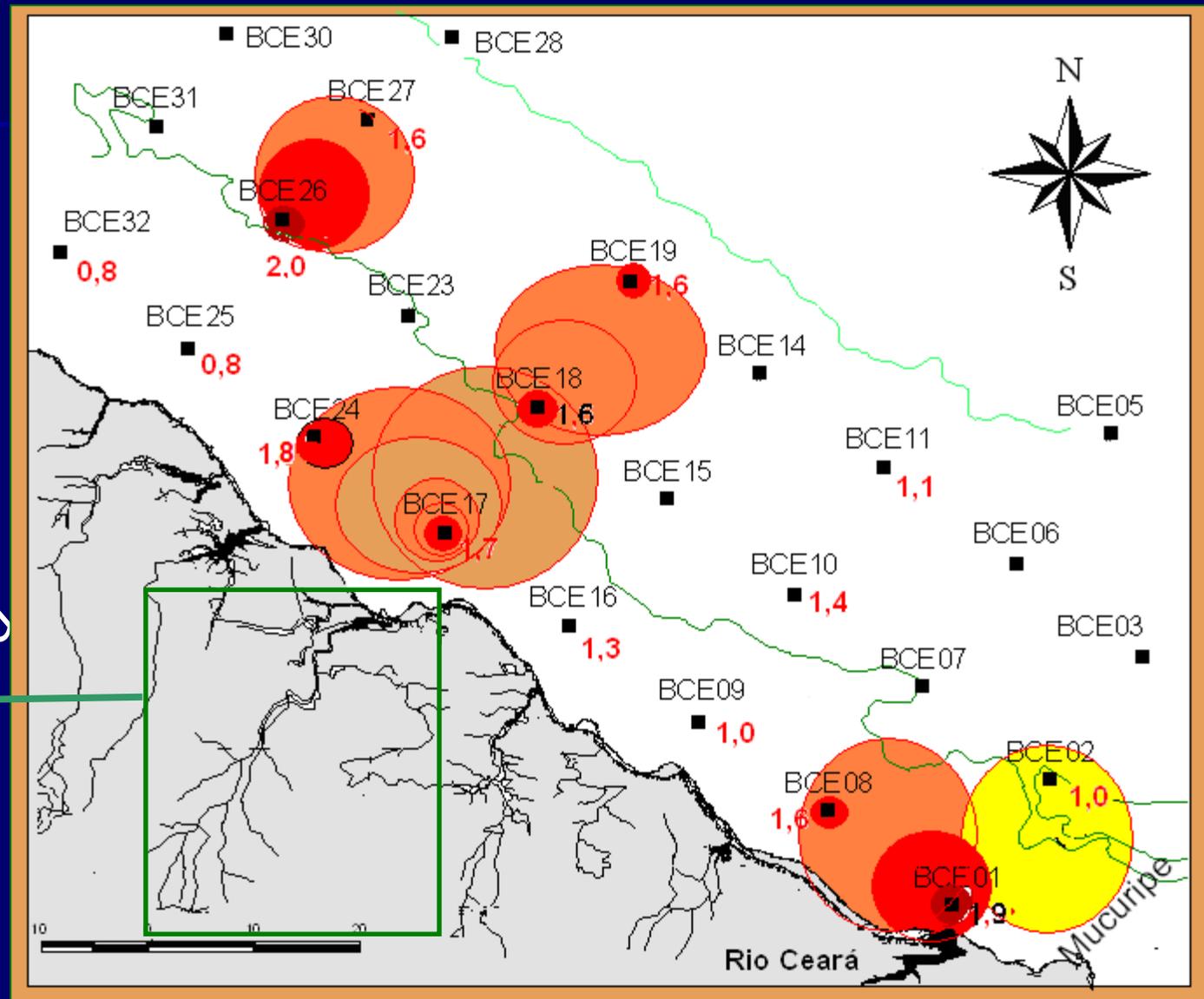


Irrigated agriculture: Vale do Acaraú (CE): metals in soils

(c.f. Lacerda & Senna, 2005, baseado em várias fontes)



The management of the area exports continental material out to shelf sediments

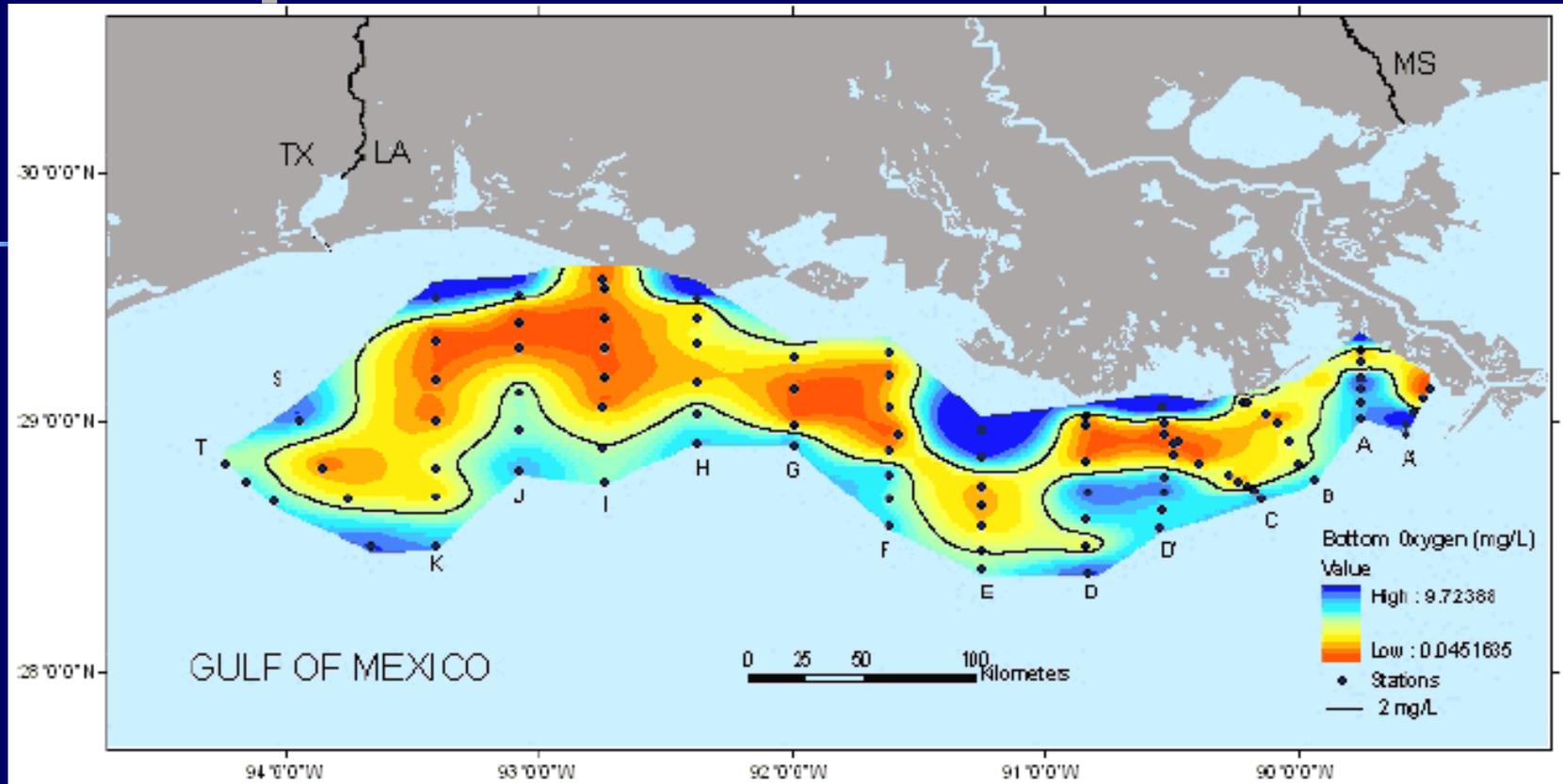


Perímetro irrigado do vale do Acaraú

A question of scale: Mississippi Delta, Gulf of Mexico, USA

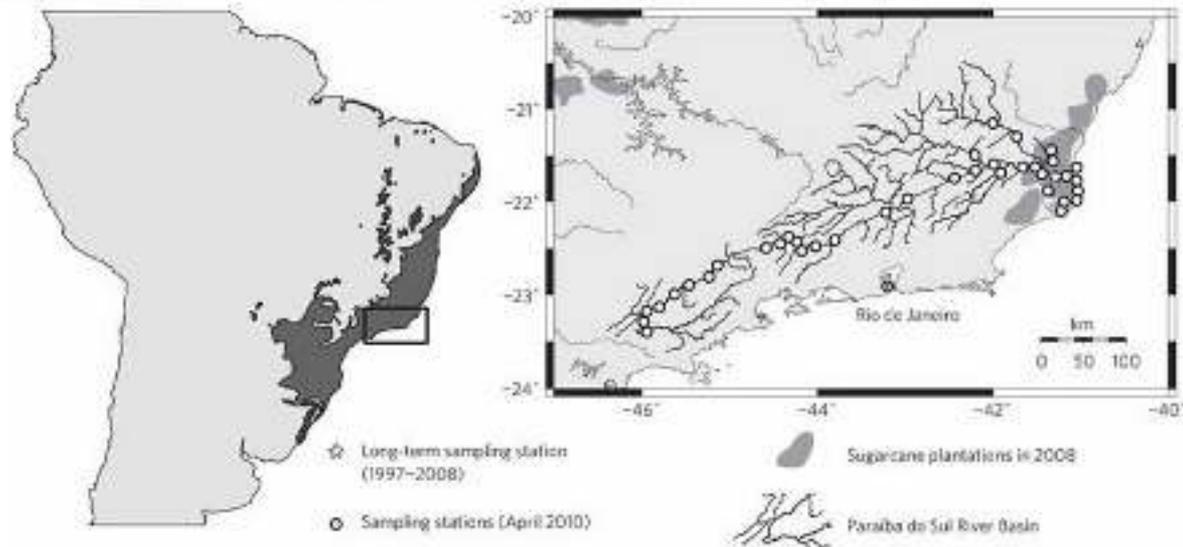


Hypoxia in coastal seas

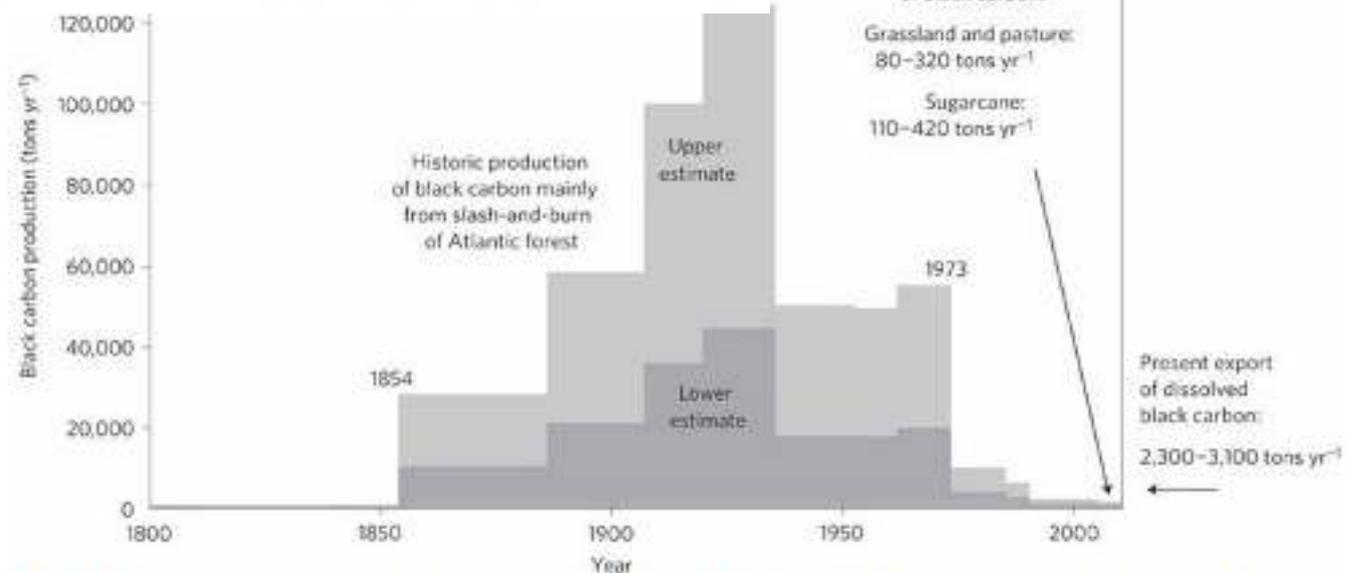


- Increasing globally due to excessive loads of nutrients and oxygen consumption
- Today, affects over 18,000 km² of the Texas-Louisiana shelf during summer

From: Continuous flux of dissolved black carbon from a vanished tropical forest biome

Continental carbon
to the South Atlantic

The original coverage of the tropical Atlantic forest in the year 1500¹ (dark shading, left panel) was reduced to about 8%, consisting of fragmented patches. Today's production (right panel) of black carbon in the drainage basin of Paraíba do Sul River (the area outlined by the box in the left panel) is largely due to pre-harvest burning of sugarcane in the lower part of the catchment area.



Annual production rates are for the polycyclic aromatic fraction of black carbon. The rate shown for the period 1800–1854 also represents the period 1500–1800. Black carbon was mainly produced by slash-and-burn clearing of the Atlantic forest. Today's production is mainly due to pasture management and pre-harvest burning of sugarcane.

Changes in land use: **Shrimp aquaculture**

(*c.f.* Marins et al., 2009)

2001

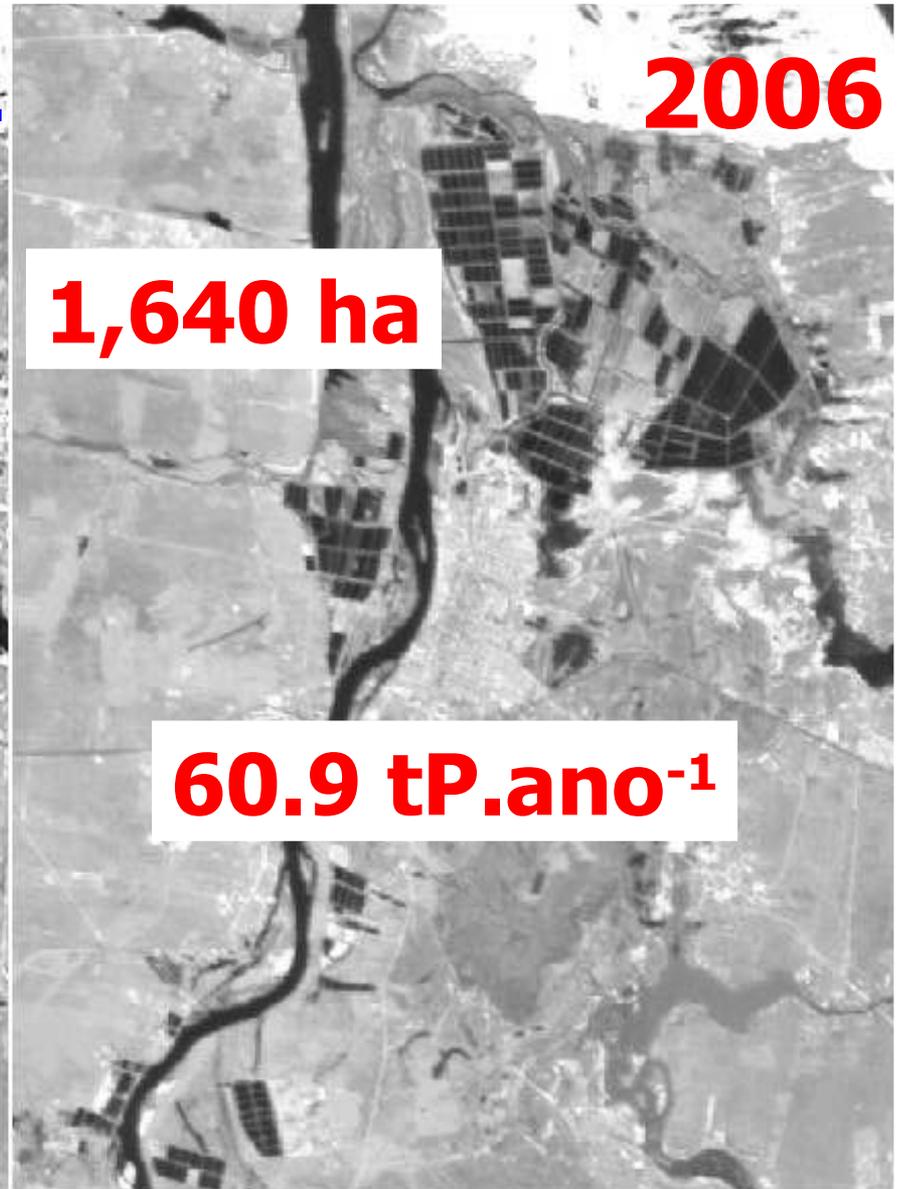
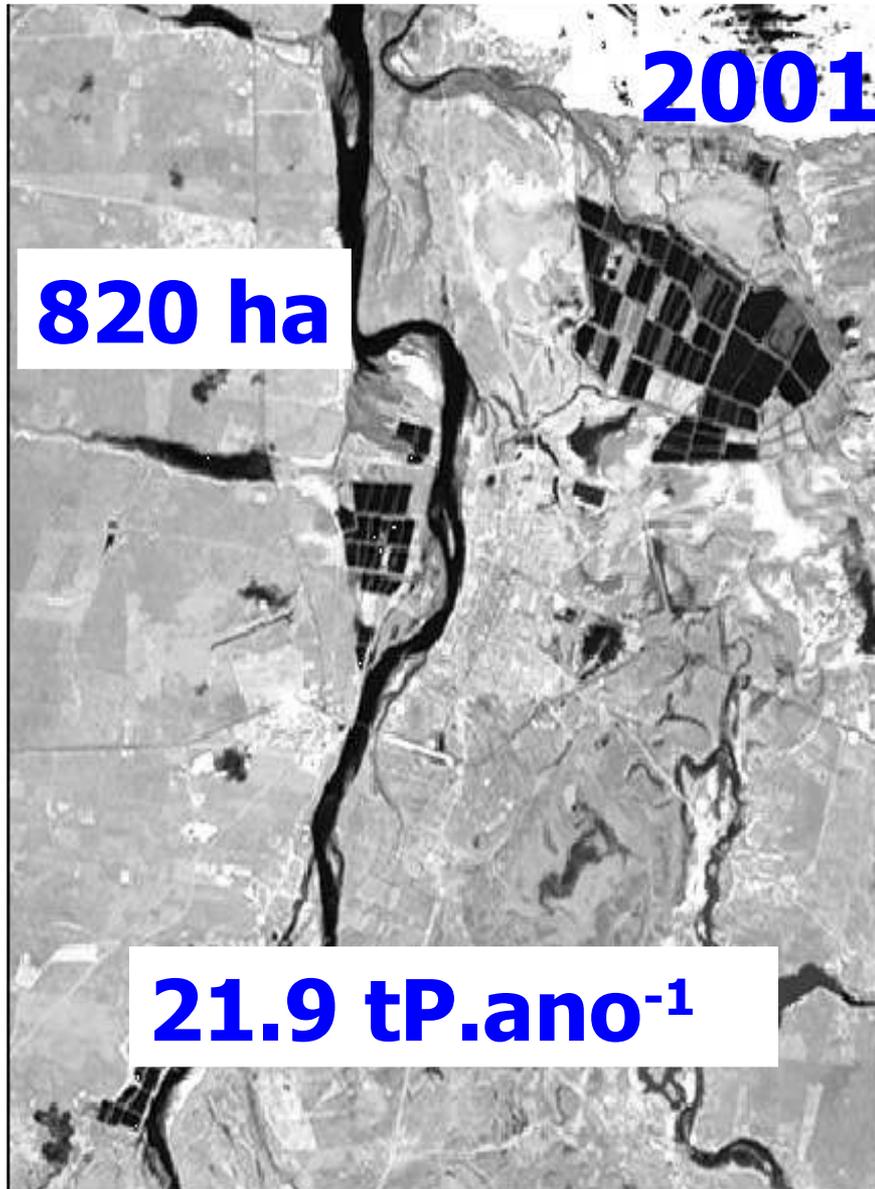
820 ha

21.9 tP.ano⁻¹

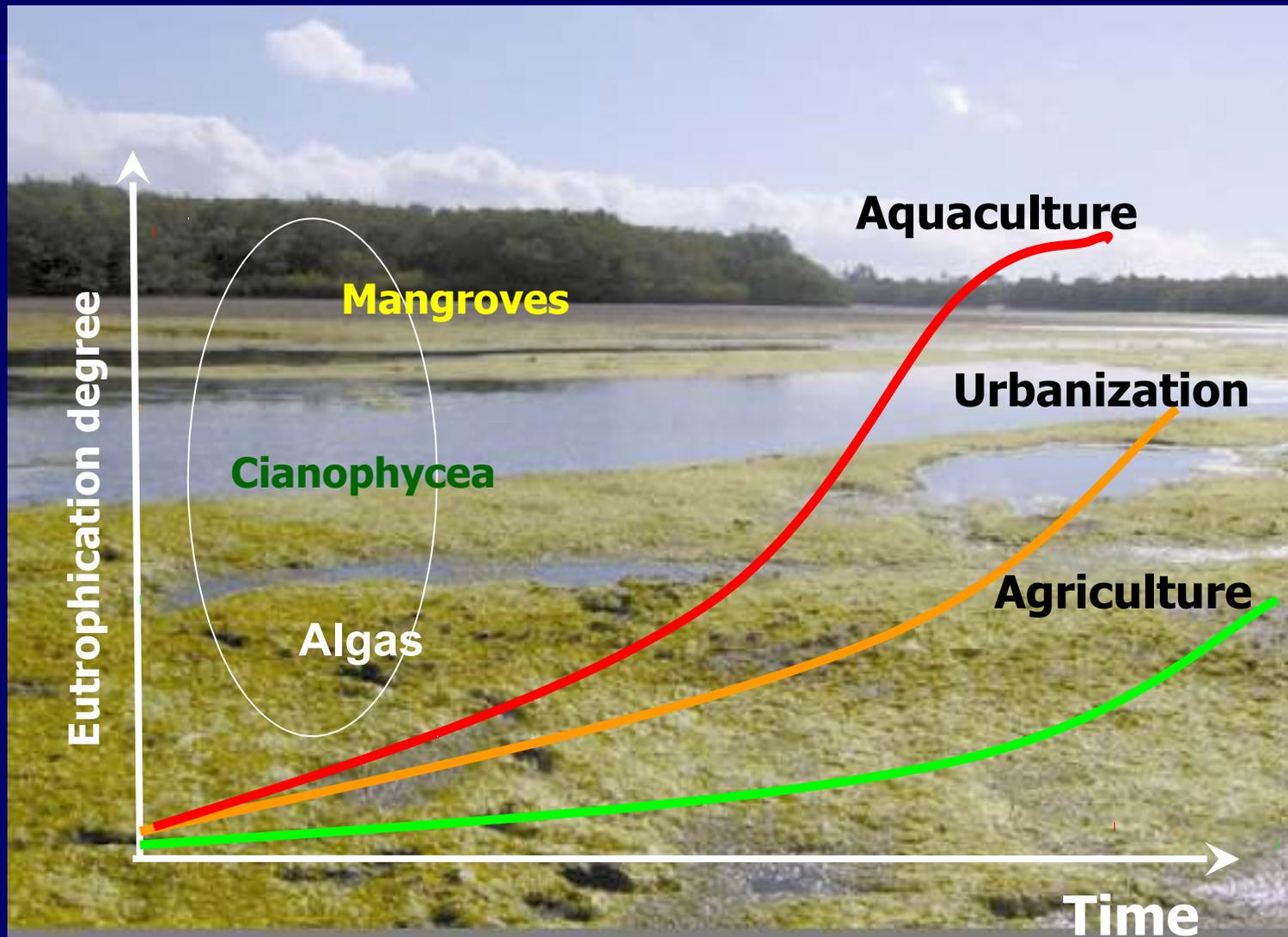
2006

1,640 ha

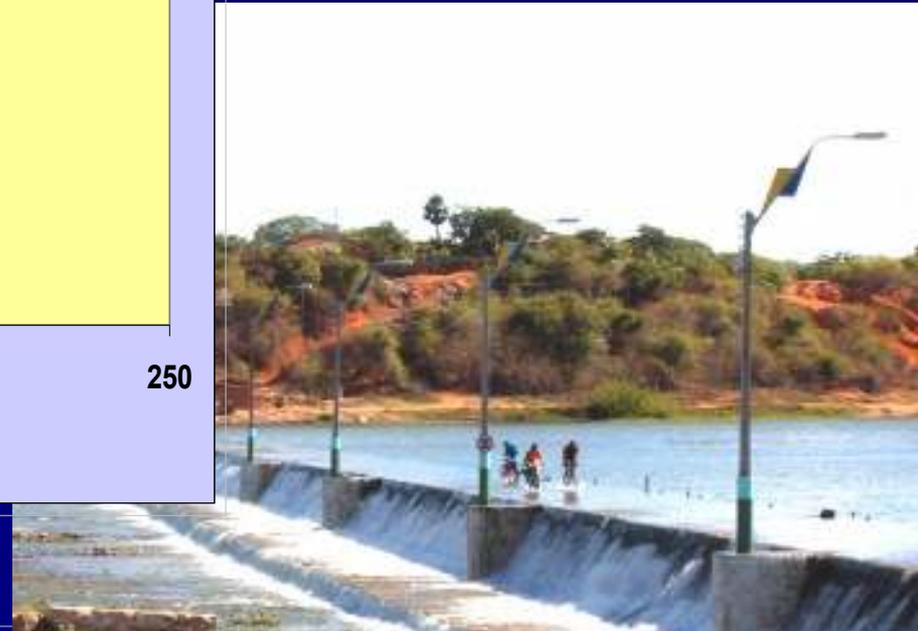
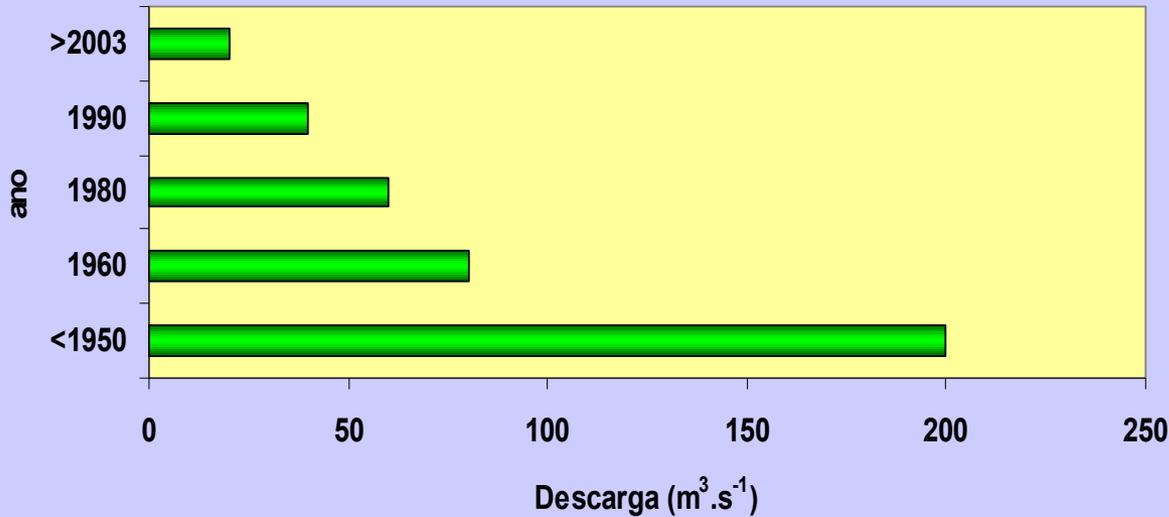
60.9 tP.ano⁻¹



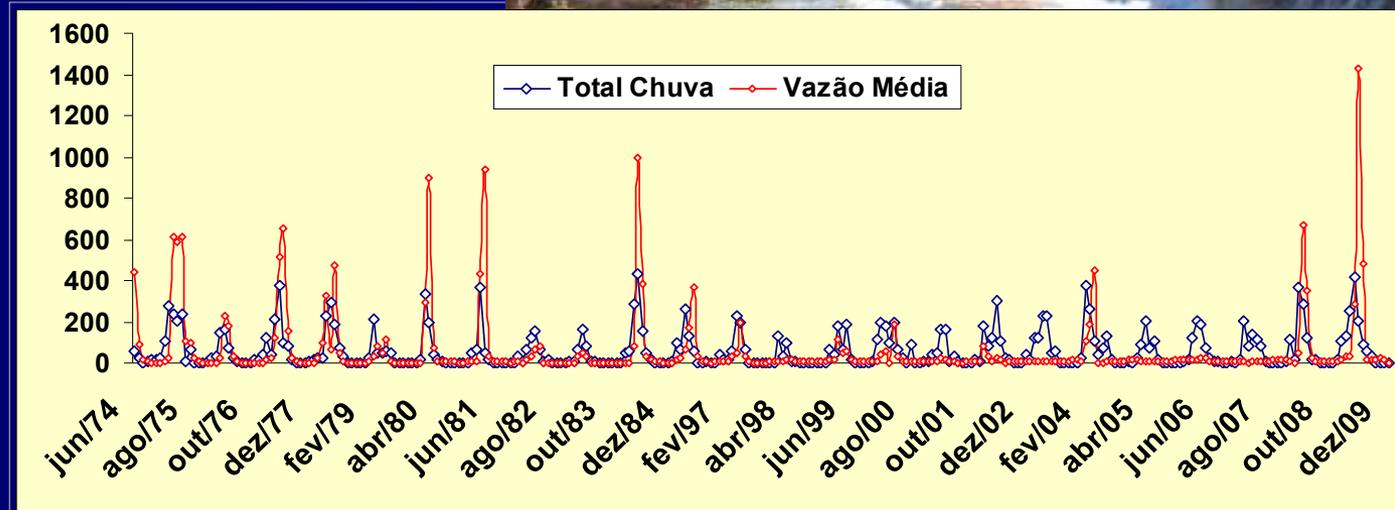
Speed of response (eutrophication) to increasing nutrient emissions from different non-industrial activities

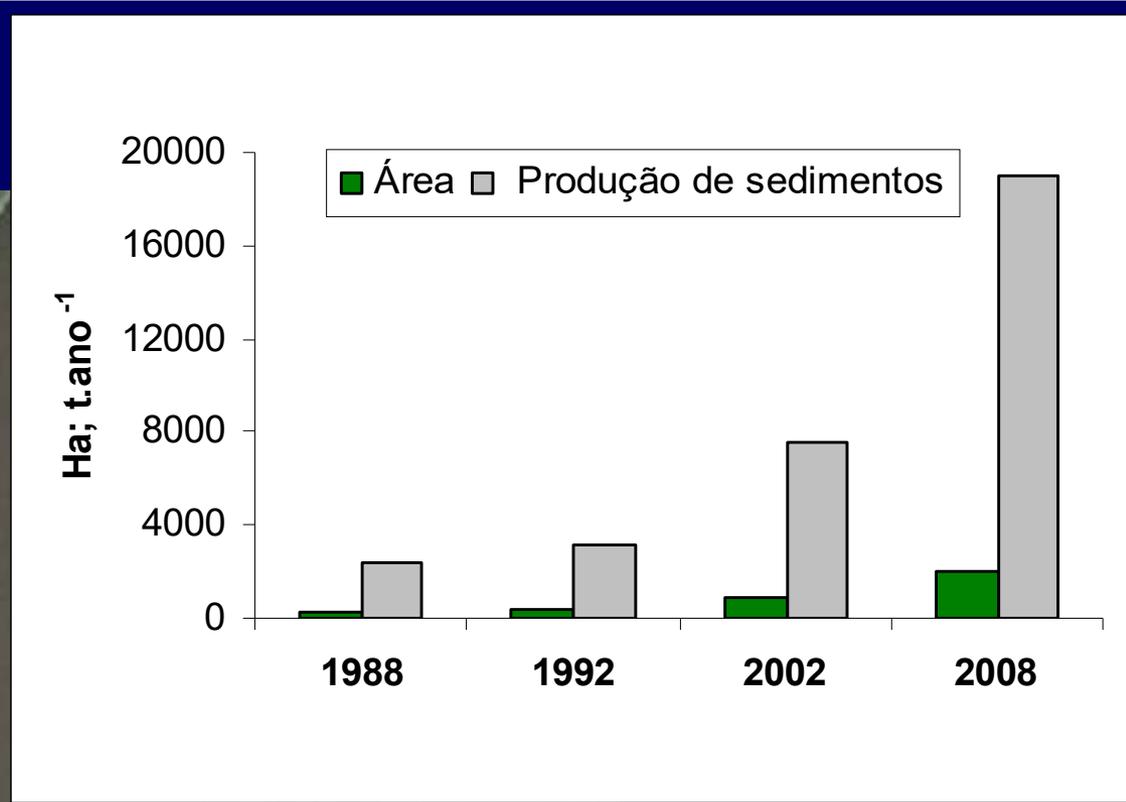
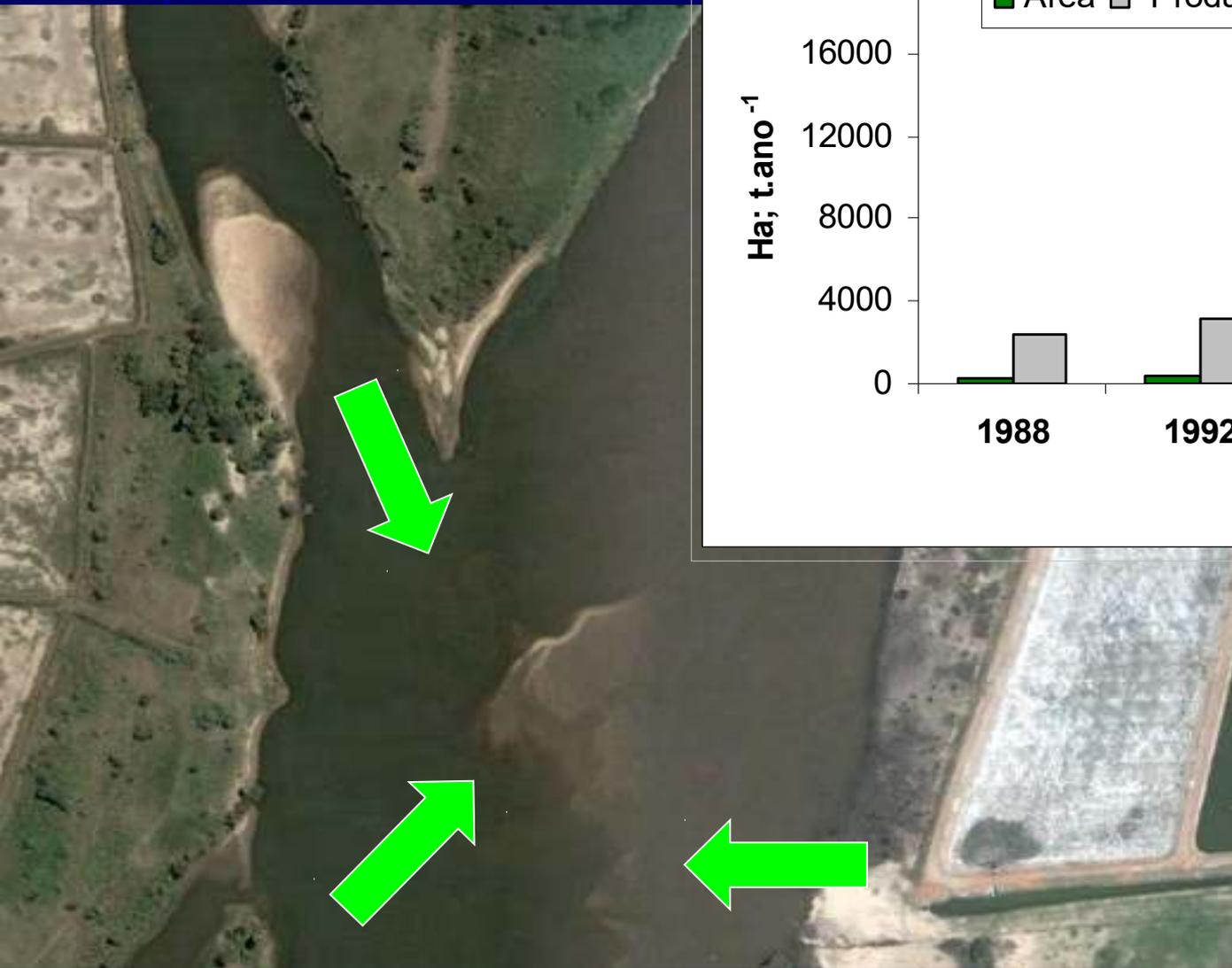


Fluxo fluvial para o Oceano Atlântico do Rio Jaguaribe, NE do Brasil durante os últimos 50 anos. (segundo Marins et al. 2002)



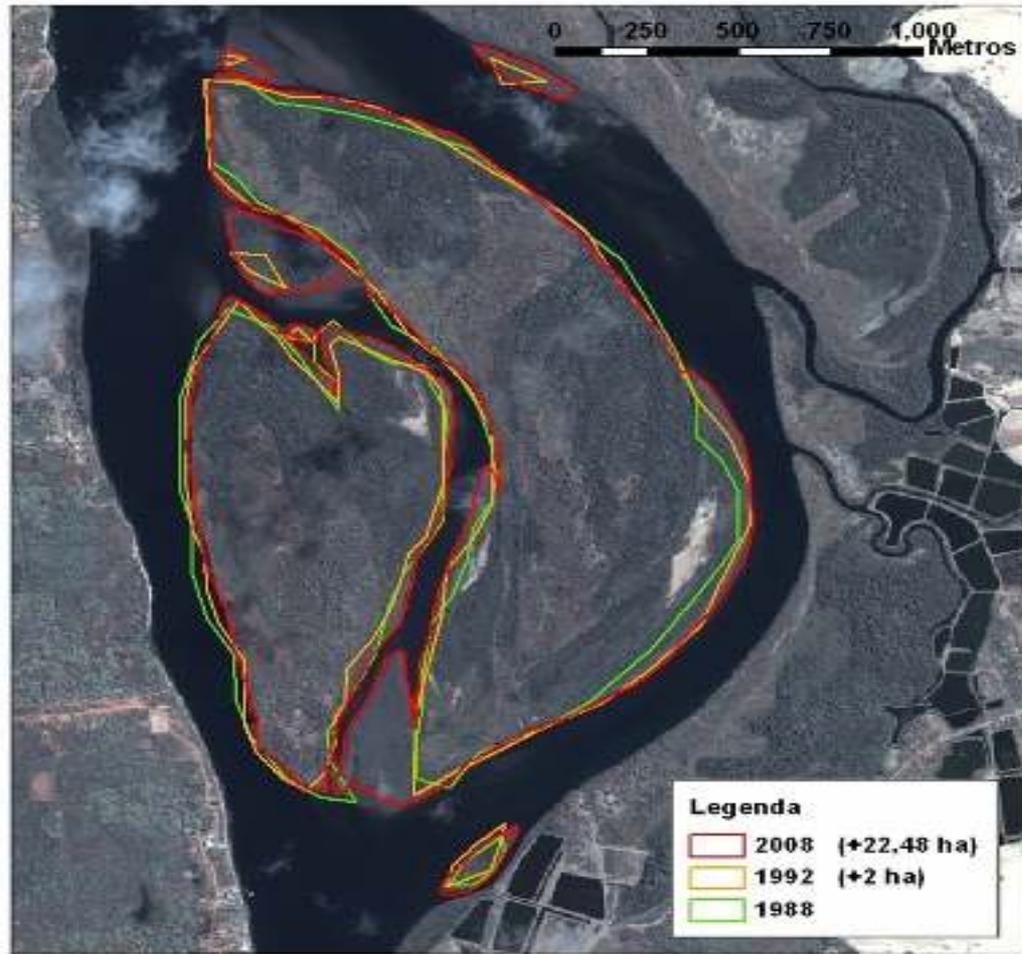
Dams





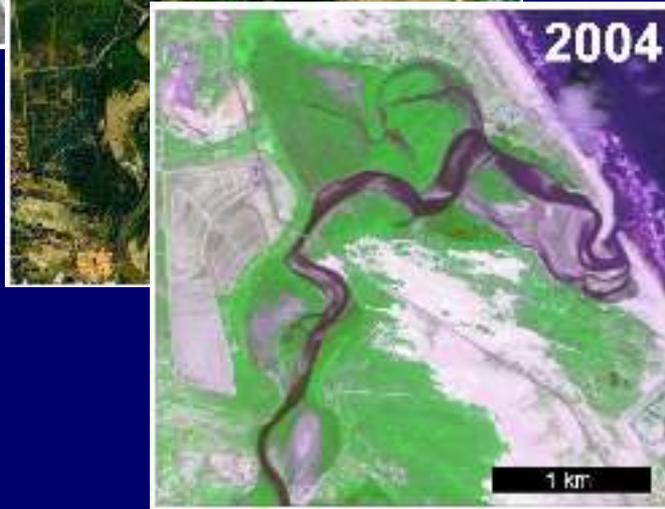
Godoy (2010)

Aquaculture & sediment production

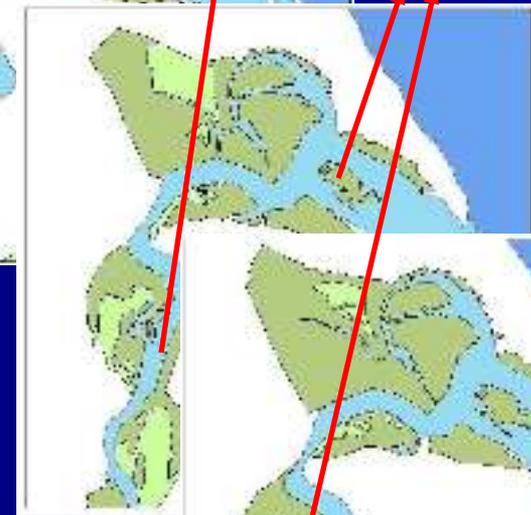
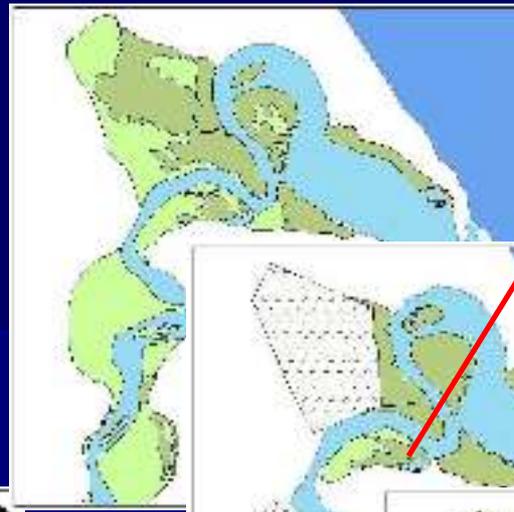


Increasing
sedimentation areas

Godoy (2010)



3.84 ha



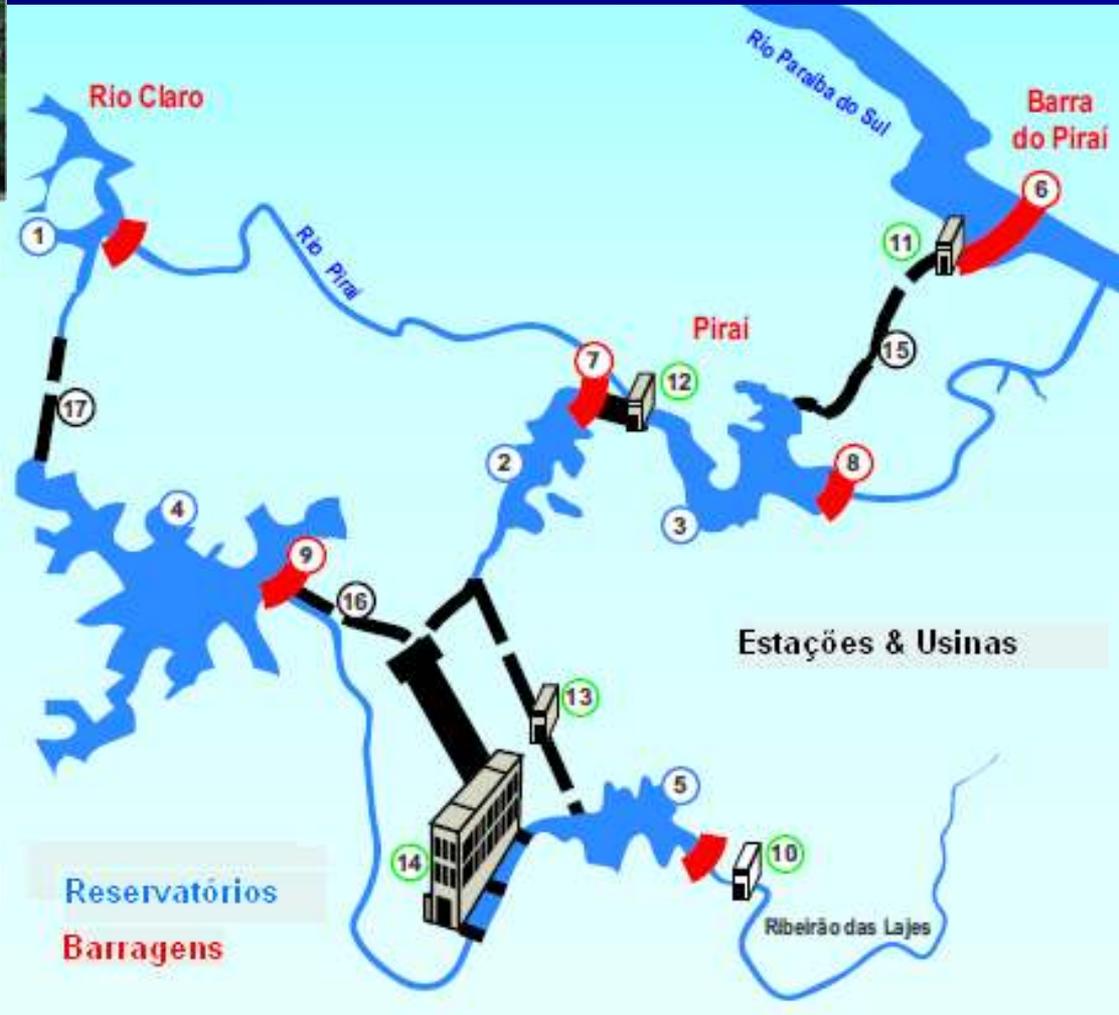
Alargamiento de
playas fluviales

Formación de
islas

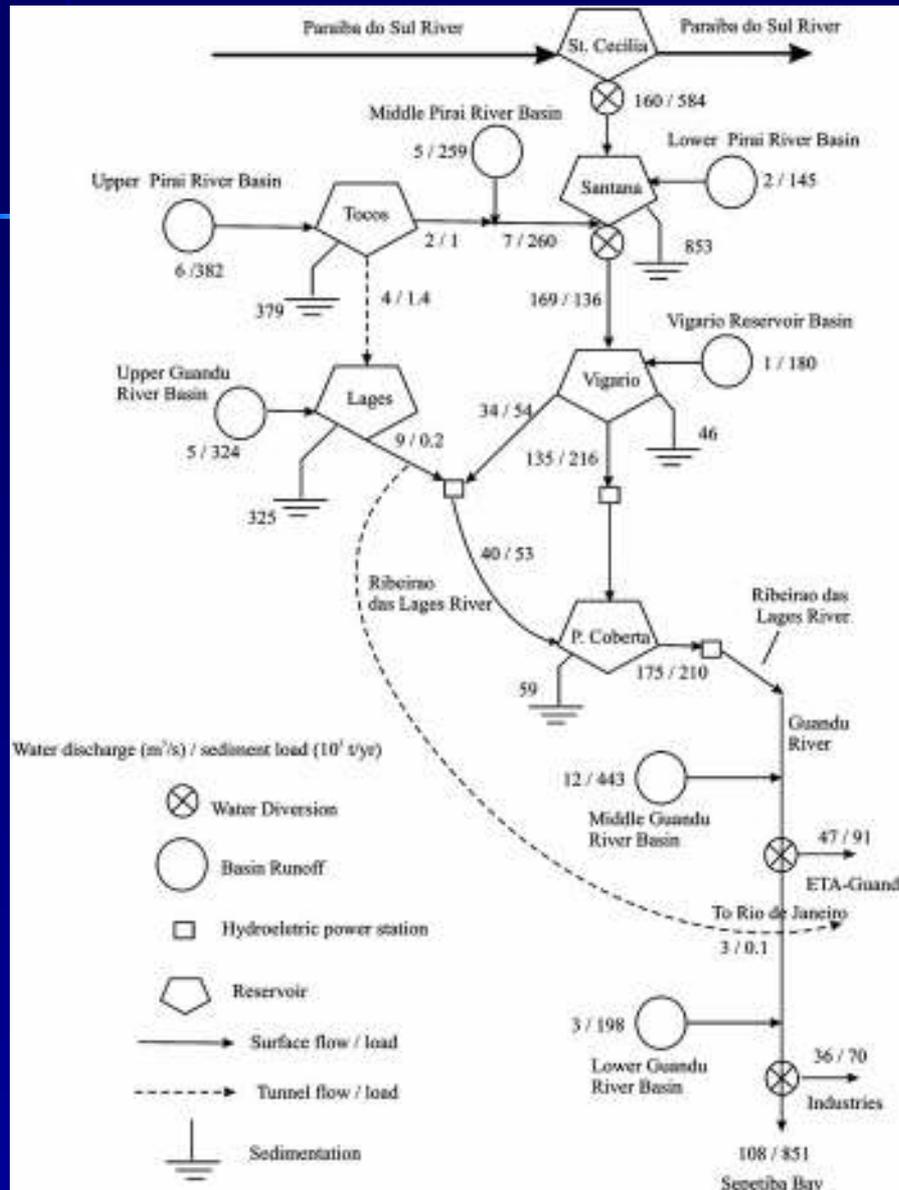
Sedimentos
Vegetación
Flujos de agua
Humedad



Water diversion



Contribuição de água e sedimentos pela transposição do Rio Paraíba do Sul para a Baía de Sepetiba

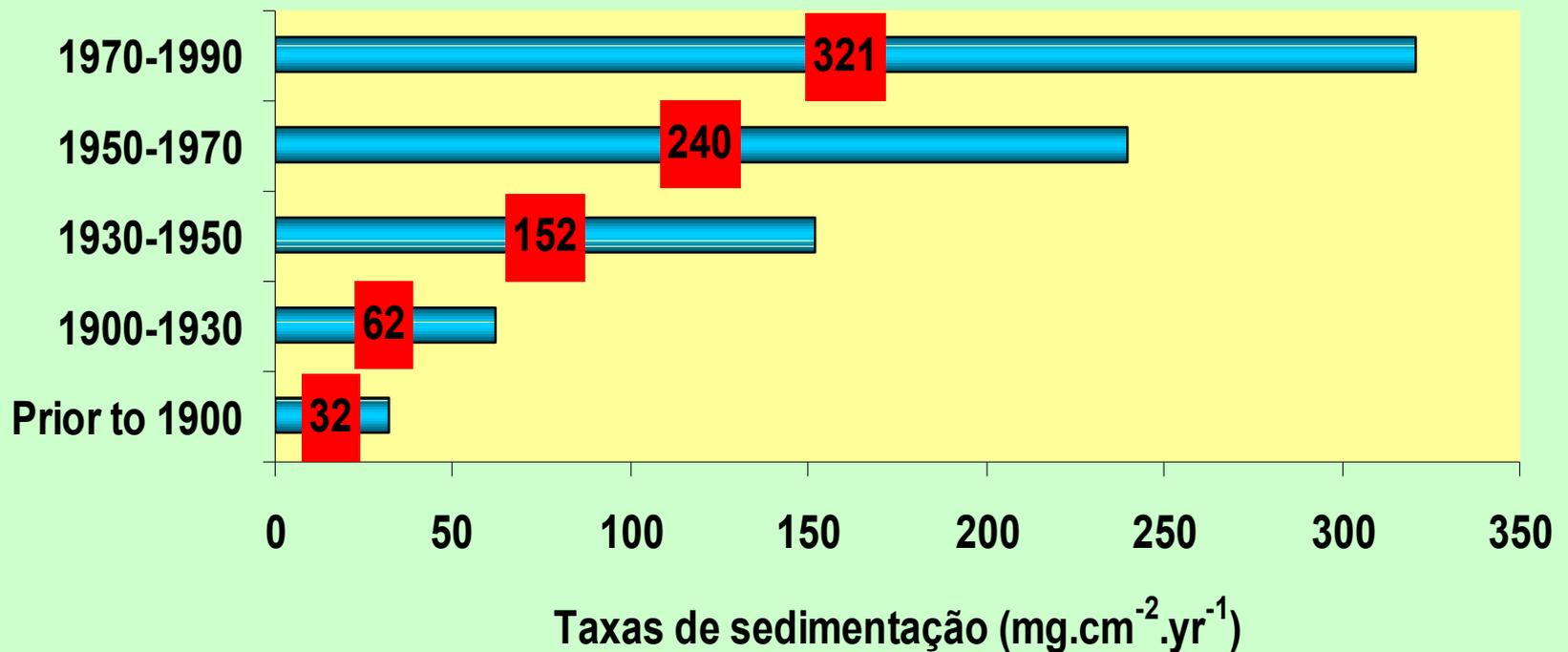


Água

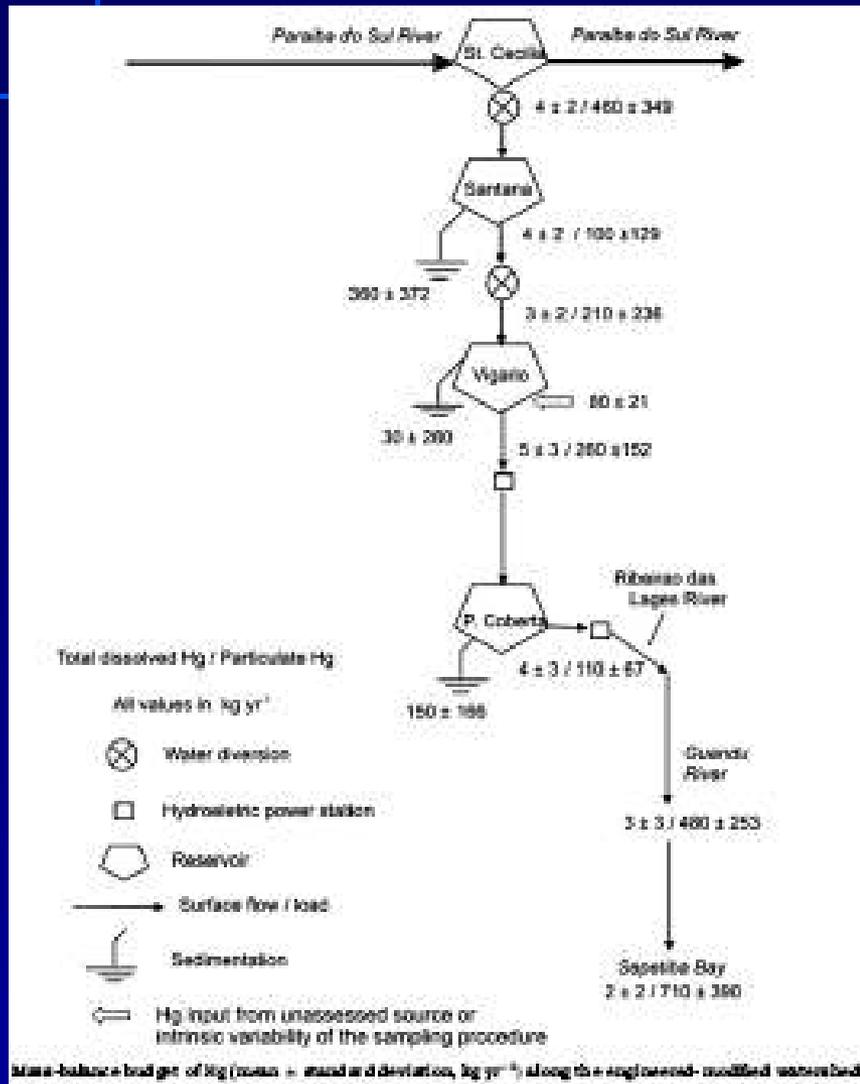


Sedimento

Mudanças nas taxas de sedimentação na Baía de Sepetiba, RJ devido a diversão de águas do Rio Paraíba do Sul (Lacerda et al. 2002)



Contribuição de Hg pela transposição do Rio Paraíba do Sul para a Baía de Sepetiba



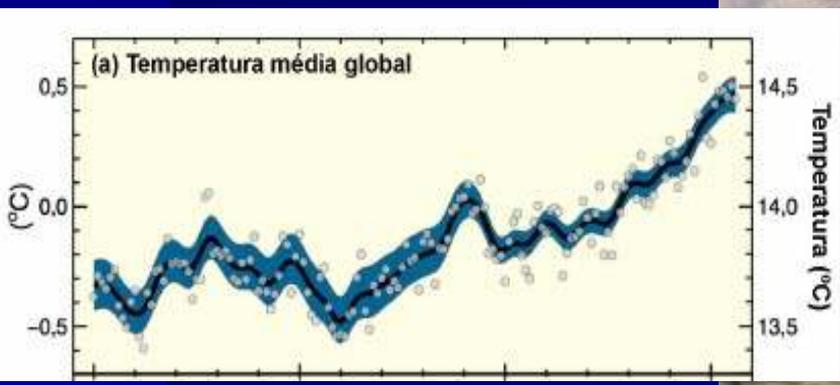
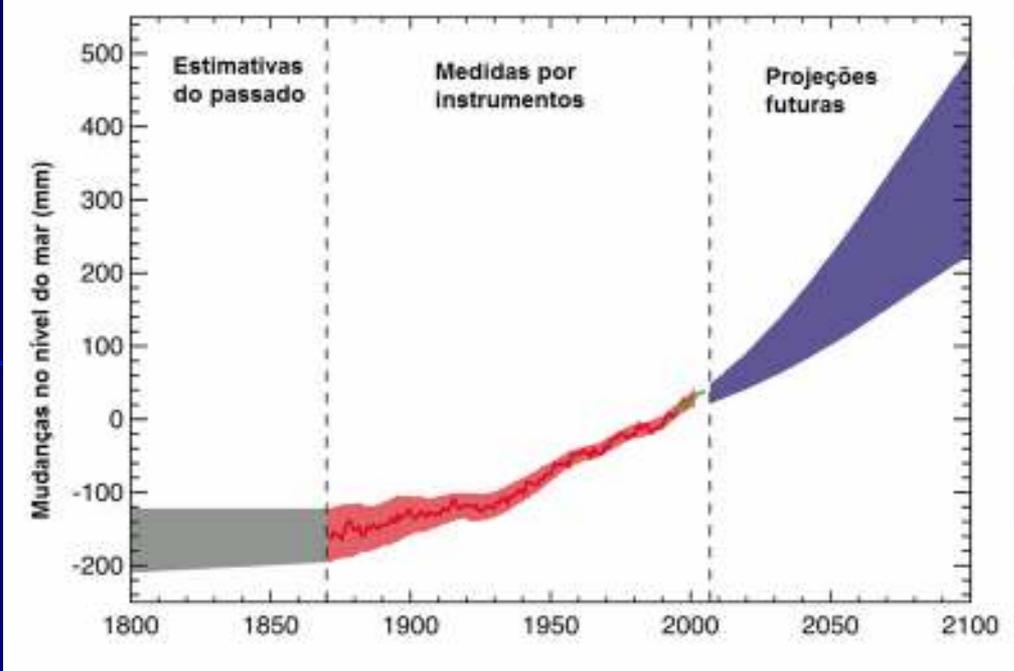
Hg-particulae



Hg-dissolved

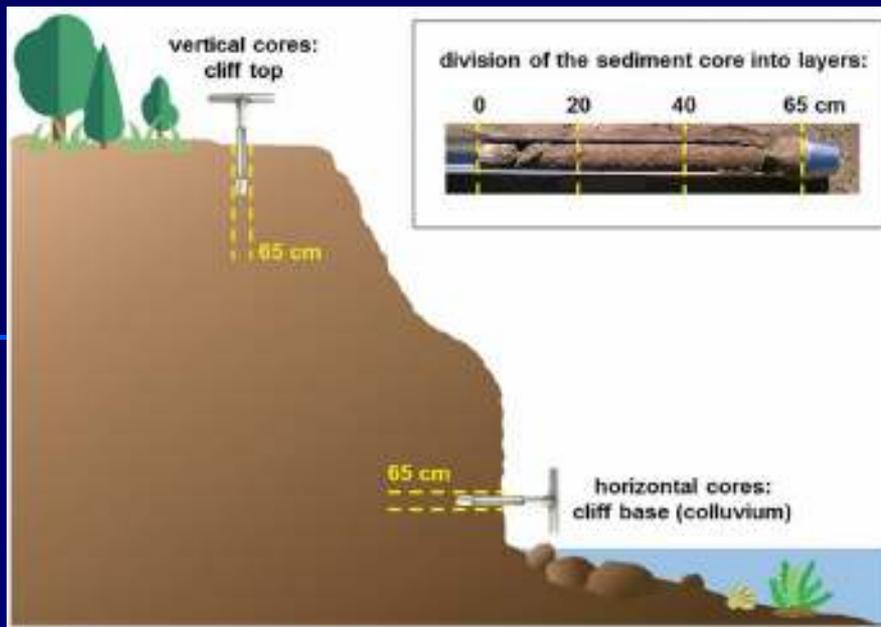
is

Global climate change: Sea level rise



Efeitos pouco óbvios: Impacto na biogeoquímica costeira

- In areas of small supply of sediments, e.g. semiarid littorals, seafront mangroves, sea cliffs; coastal deposits are increasing the remobilization of pollutants.
- On the other hand, coastal plain areas in the tropics and subtropics dominated by mangroves, sea level rise will induce mangrove migration inland, creating typical areas dominated by the mangrove metabolism (e.g. anerobic respiration through sulfate reduction).
- Trace metal biogeochemistry and bioavailability are highly affected by the sulfate reduction metabolism.
- Part of the metal load will be accumulated as metallic sulfides in sediments, but part, with the abundant dissolved organic carbon compounds due to incomplete oxidation of organic matter, will be made more bioavailable, increasing bioaccumulation and enhancing biota and human exposure through food chains.



Sea level rise and Hg contribution through erosion
 (Kwasigroch et al., 2018 (in press))
 Up to 14.5 kg.yr^{-1} ; the 3rd most important Hg source to Gdansk Bay.

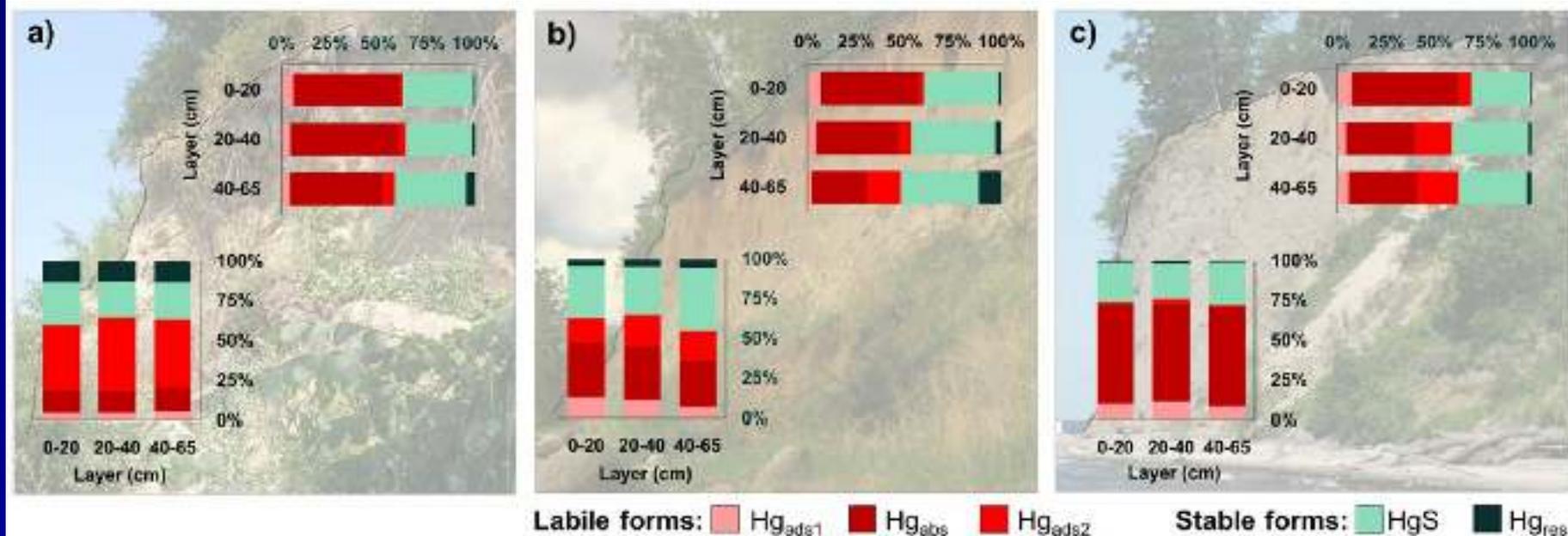


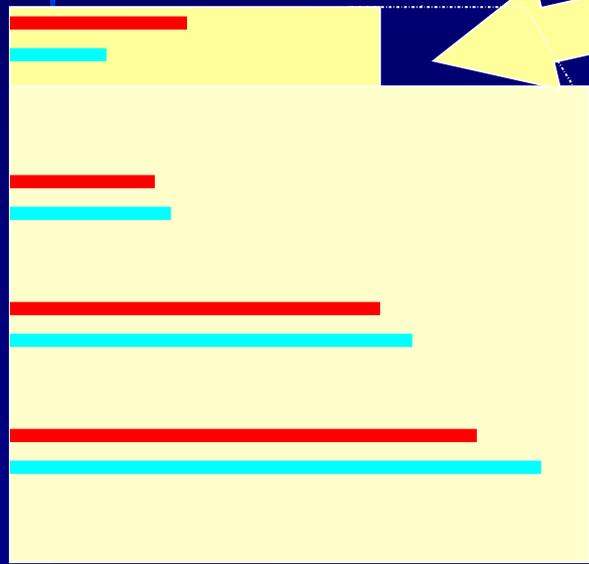
Fig. 3 The percentage of Hg fractions in horizontal and vertical profiles of investigated cliffs. a Puck cliff, b Osłonino cliff, c Mechelinki cliff

Erosion of coastal mangroves sediments in NE Brazil



Metal concentrations ($\mu\text{g/g}$)

2x 4x 6x 8x ?



— Metal A — Metal B

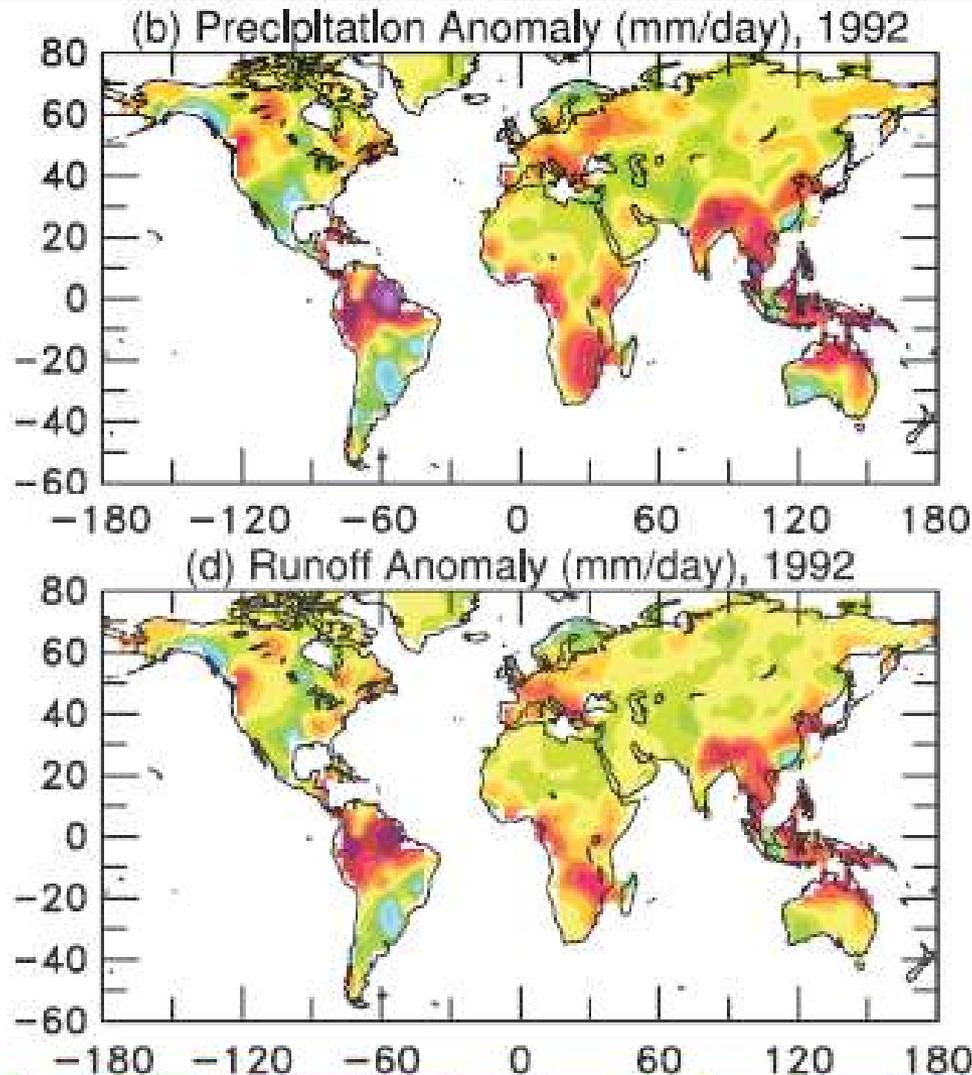
RIVER



Variação do escoamento superficial e precipitação global

Out of 200 rivers, **45**, mostly in lower latitudes, have their flows decreased between 1984 and 2004, whereas **19**, have them increased

Increasing fluxes are frequently in higher latitudes and increasing flux **do not relates to increasing rainfall**, a probable reflect of ice and glacier melt.



Dai et al., 2009)



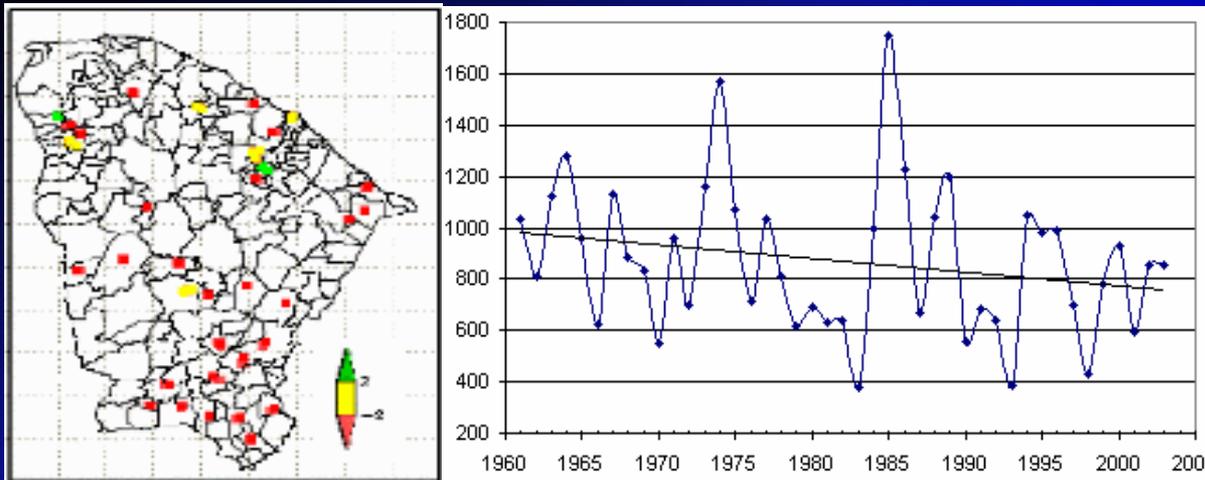
Reduction Annual precipitation and runoff anomalies

Rainfall reduction in Ceara, NE Brazil

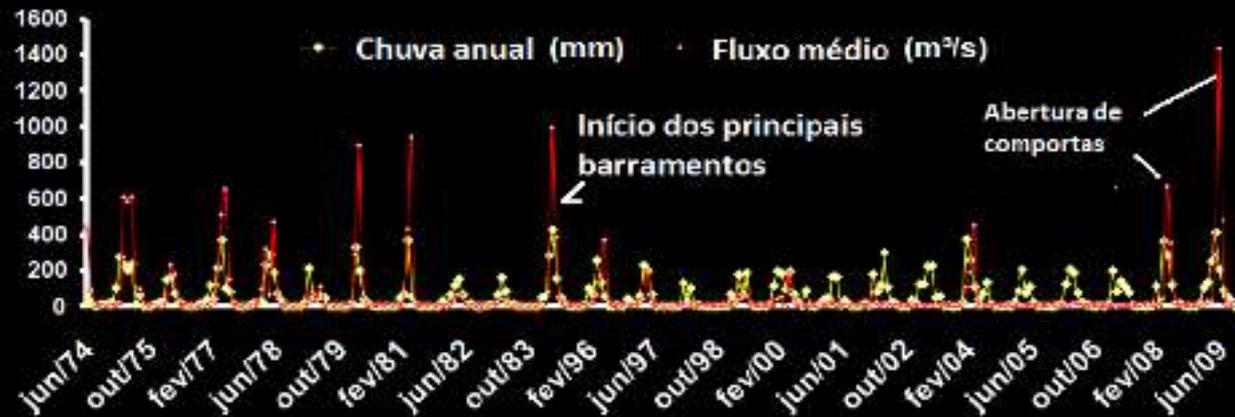
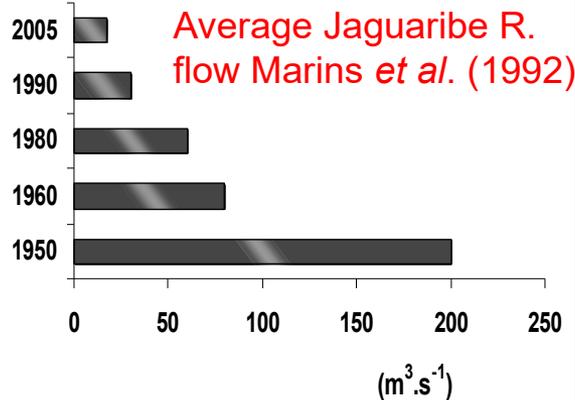
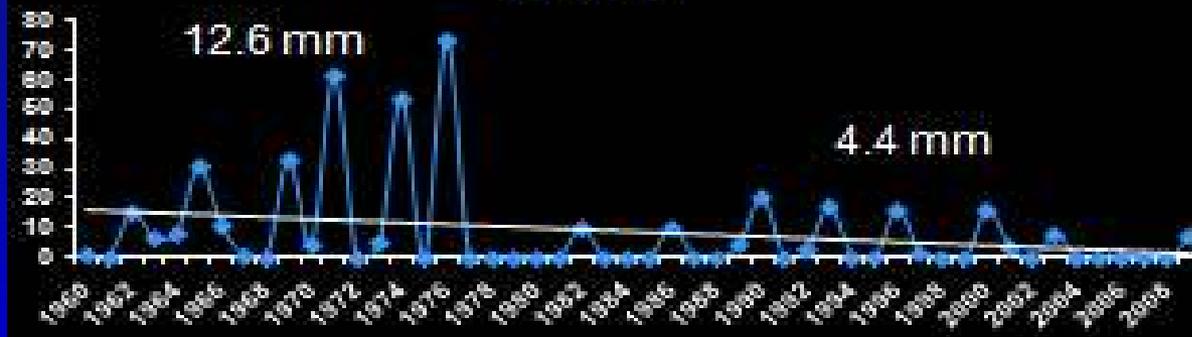
Evolution Trend (1961 – 2008) in annual precipitation over Ceará. (4 - 5 mm.yr⁻¹ reduction) (Moncuil, 2006).

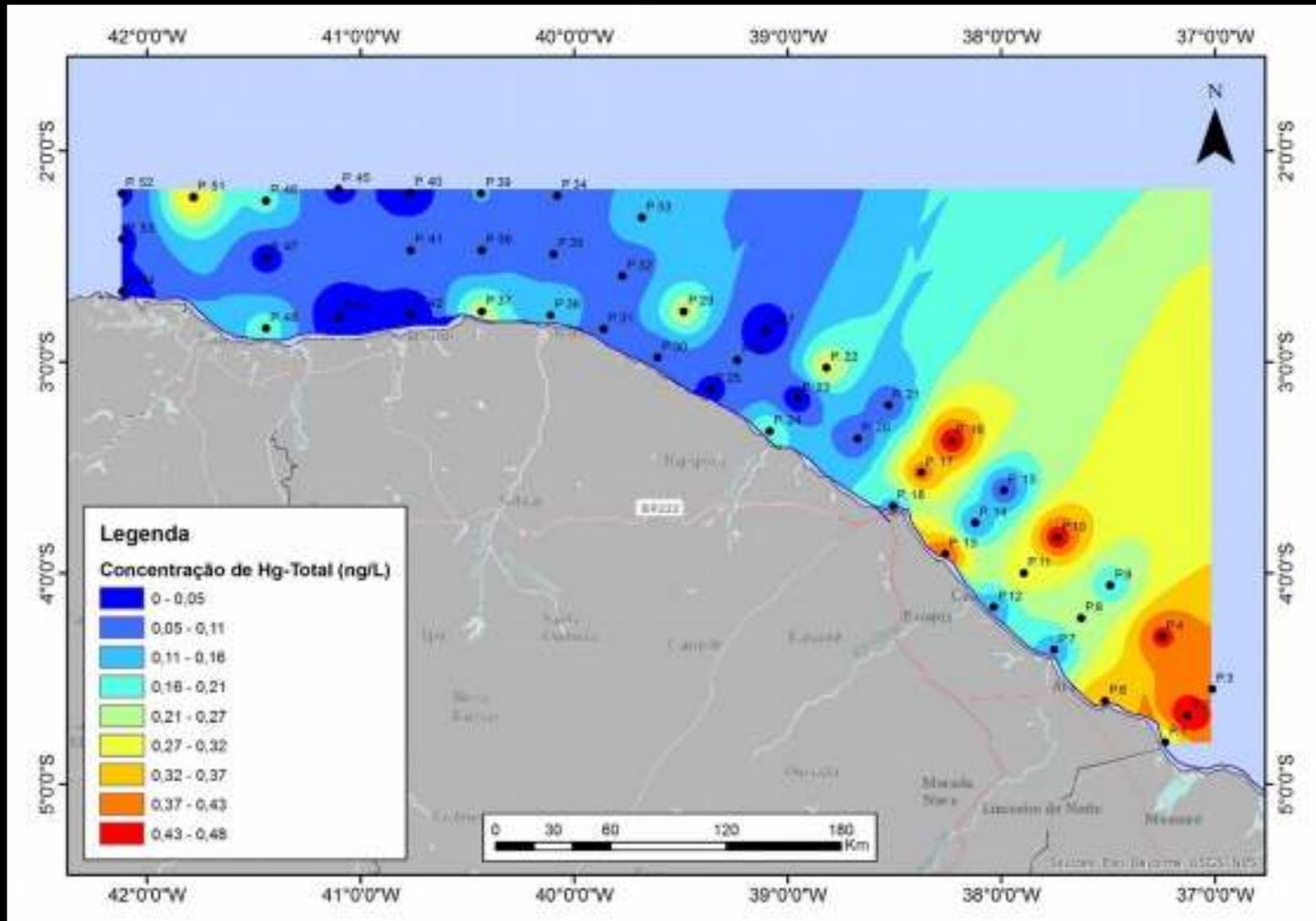
Reduction is more critical (3 times) during the dry season (Godoy *et al.*, 2010)

River discharges also decrease and are further affected by damming (Godoy *et al.*, 2010)



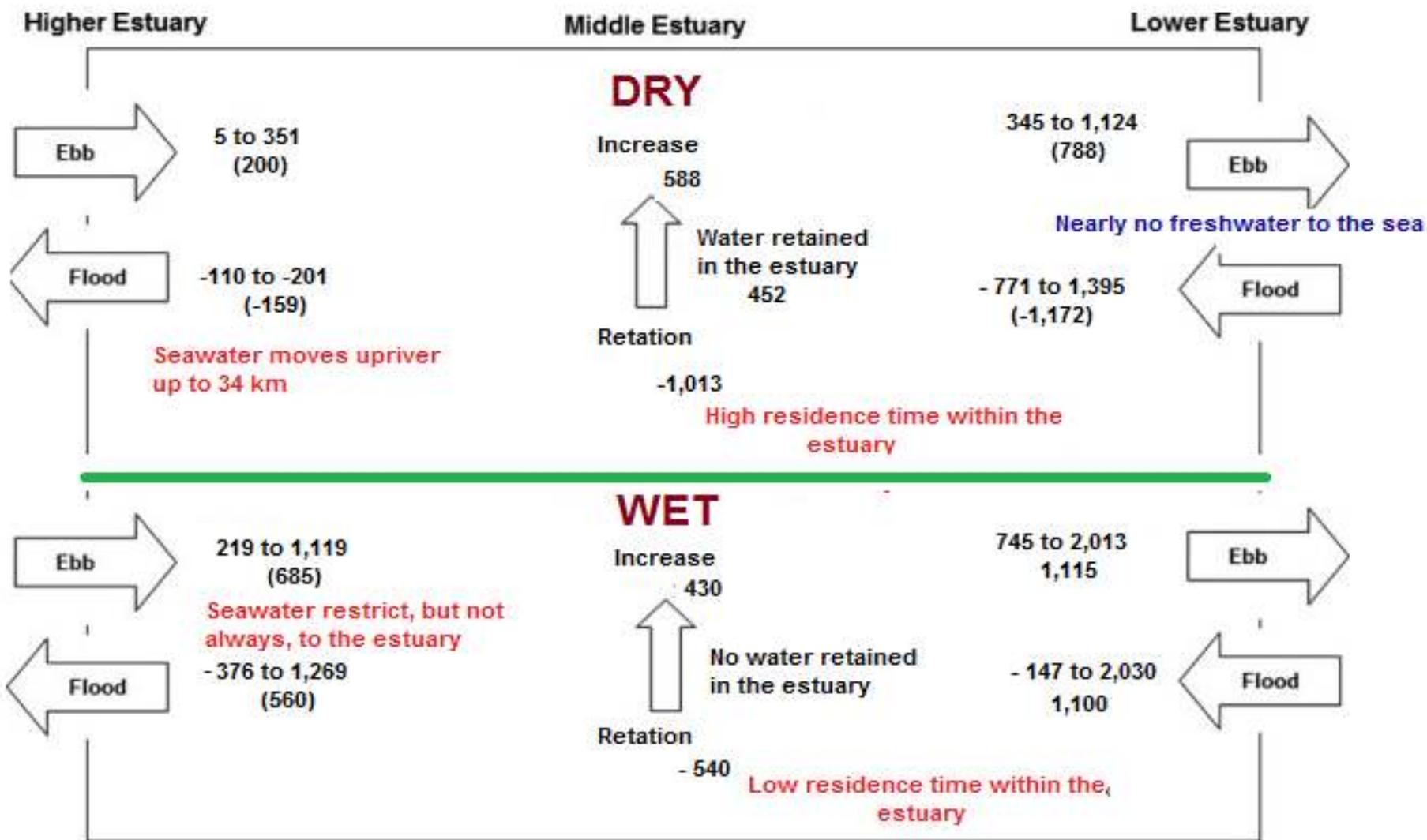
Aracati





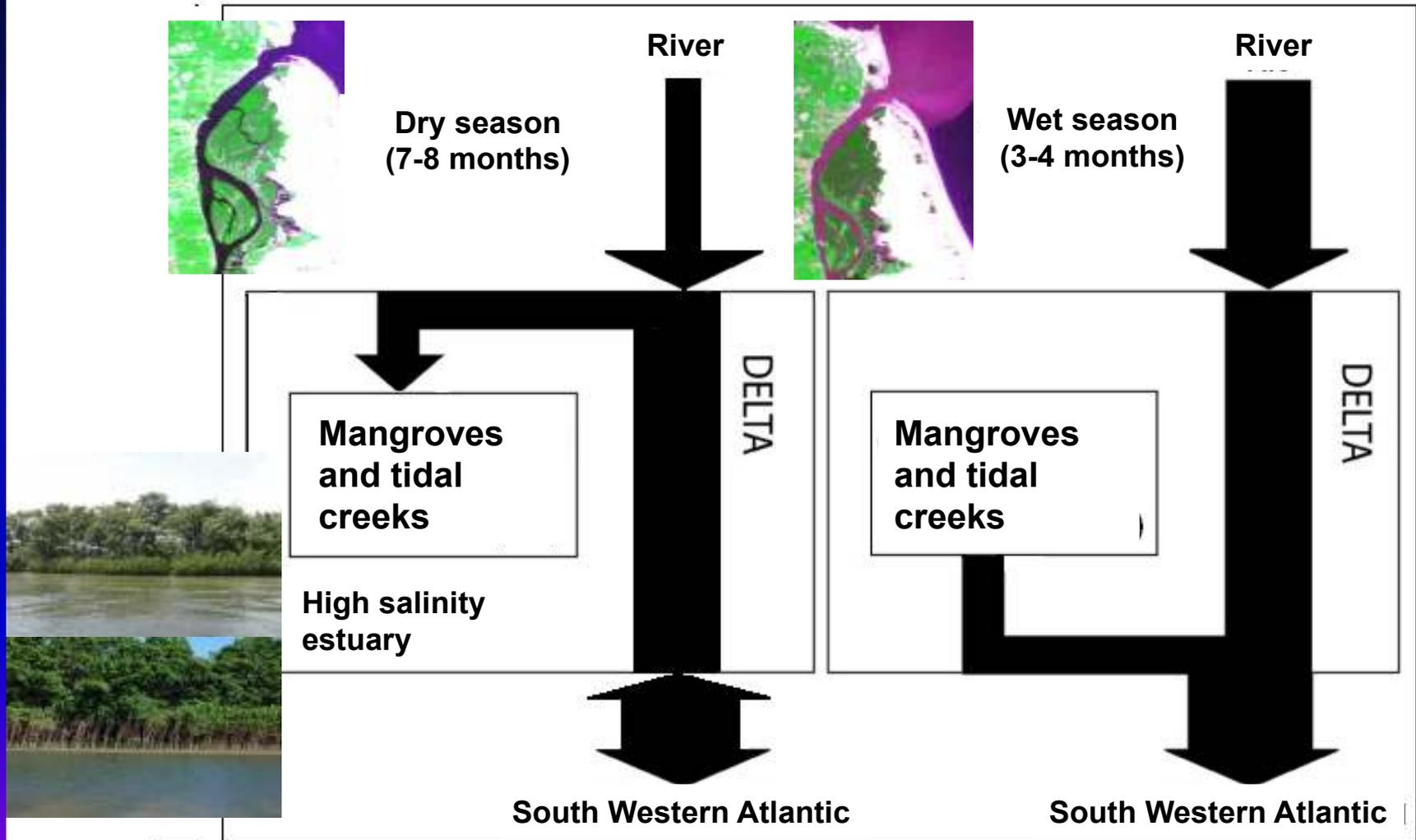
Mercury distribution in coastal waters of the semiarid northeast as a proxy of regional changes in the NE region's watersheds. The clear pattern of higher concentrations to the east are a result of such changes.

Water balance ($\text{m}^3 \cdot \text{s}^{-1}$) at the Jaguaribe estuary, NE Brazil (Dias, Lacerda & Marins 2011) pluriannual average.

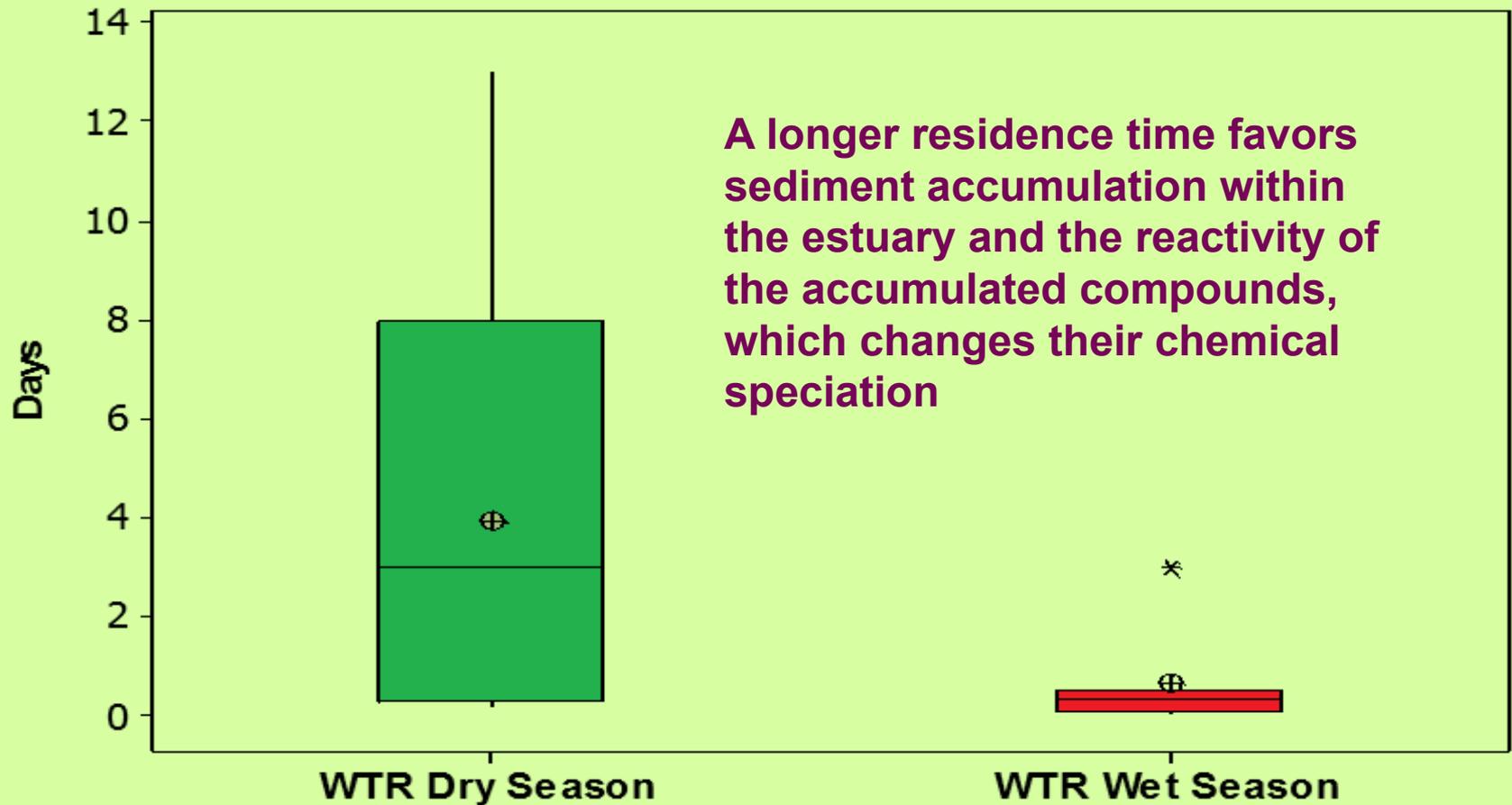


Water balance in the Jaguaribe Estuary (2001-2013)
 $\text{m}^3 \cdot \text{s}^{-1}$

Conceptual hydrodynamics model of semi-arid rivers, from Lacerda , Marins & Dias (2012)



Choking of the lower estuary due to decreasing continental runoff and increasing the strength of ocean forcing over the continental shelf, results in longer residence time of water masses within the estuary during the dry season (Lacerda, Marins & Dias, 2012)



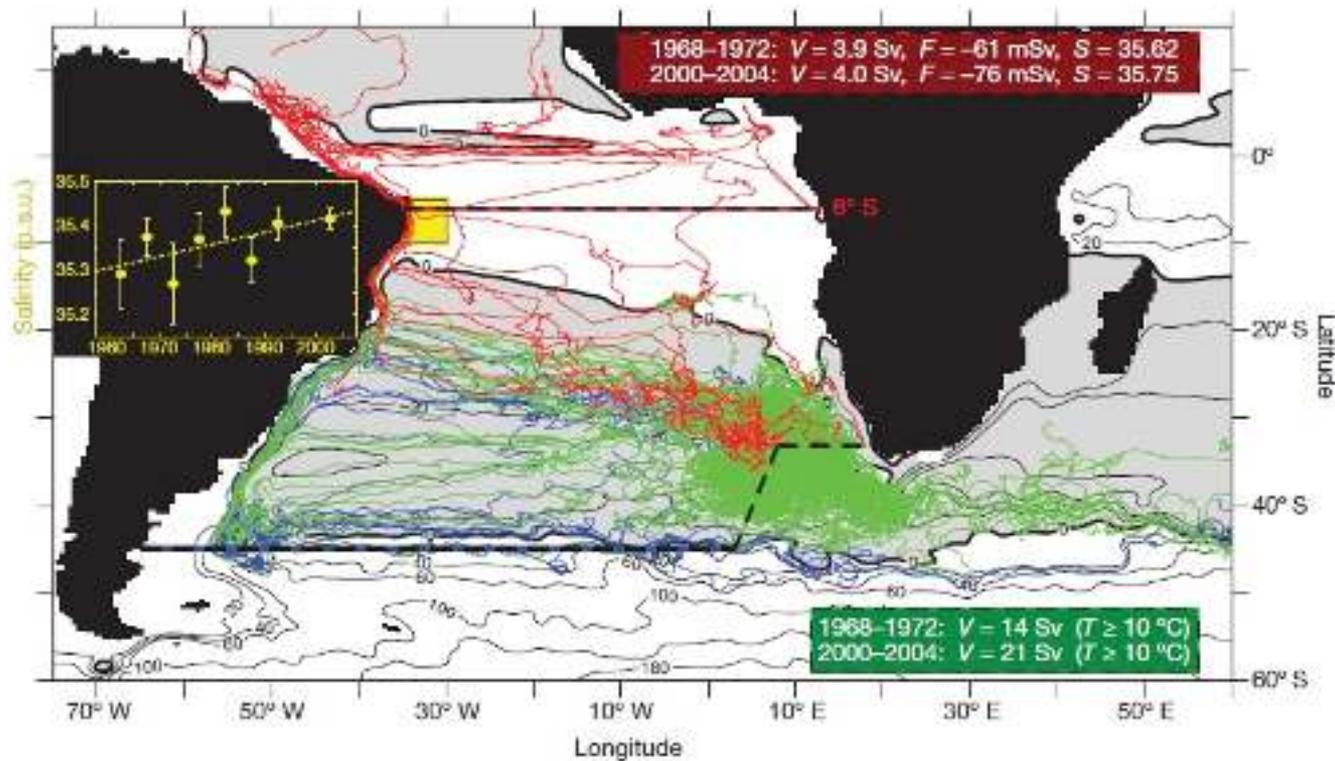
The hydrodynamics of rivers in the semi-arid at the continent - ocean interface and therefore the distribution and biogeochemistry of their ecosystems depends on:

- 1 – the magnitude of the fluvial flux & continental runoff;**
- 2 – the residence time of water masses in flooded areas and;**
- 3 – sea level variation and the volume of the tidal prism.**

All these variables are highly sensitive to global climate change.

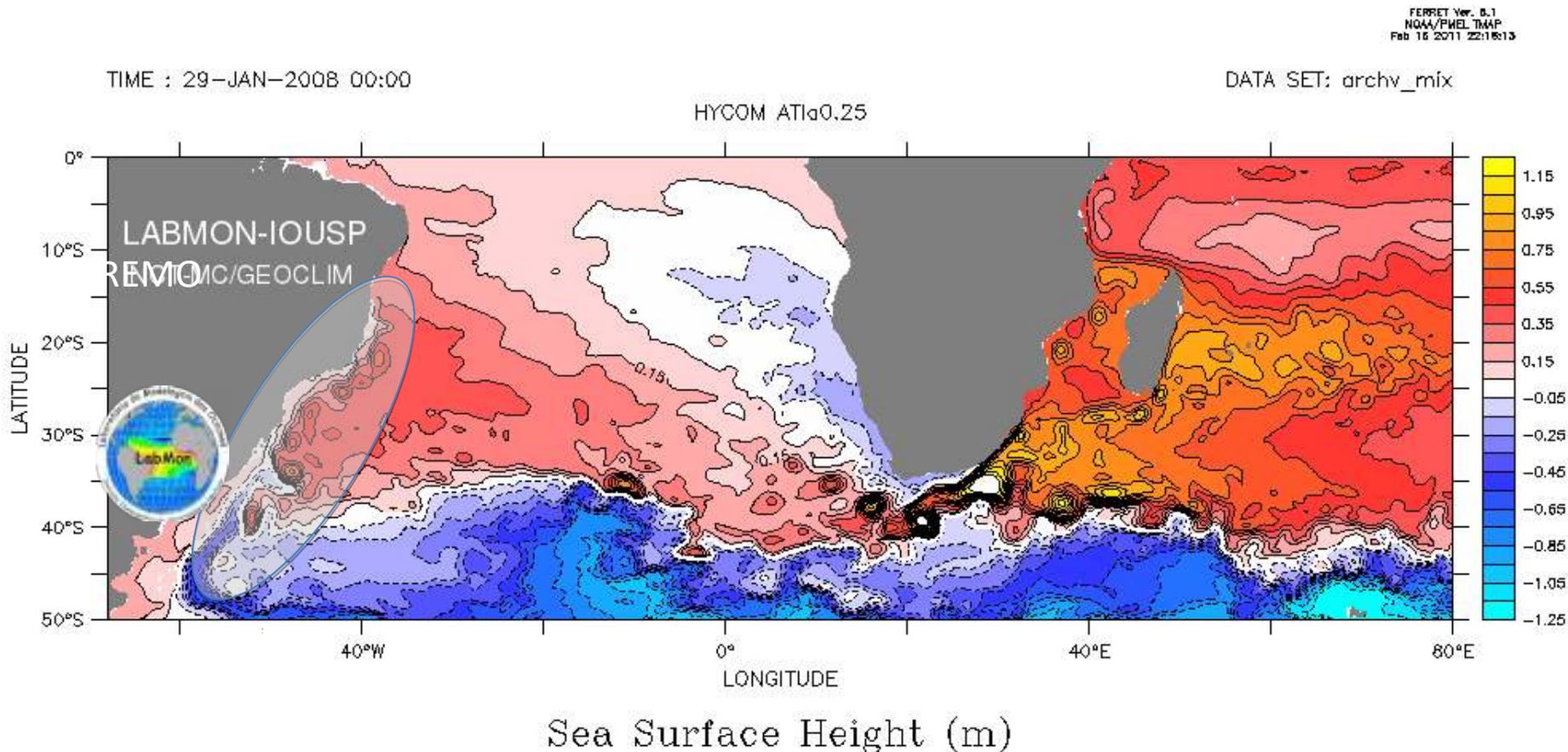
Therefore, how global climate change is already affecting the functioning of the semi-arid ecosystems and what can we expect in the future?

Apart from the effects of global and regional changes at the semi arid region itself, tele-connections & large scale transfer in the South Atlantic Ocean may also affect the residence time in estuaries and eventually the export and mobility of substances to marine food chains.



E.g. The increasing strength of the Agulhas leakage (*Biastoch, A., C.W. Böning, F.U. Schwarzcopf and J.R.E. Lutjeharms, Nature 462, 495-498, Nov/2009*).

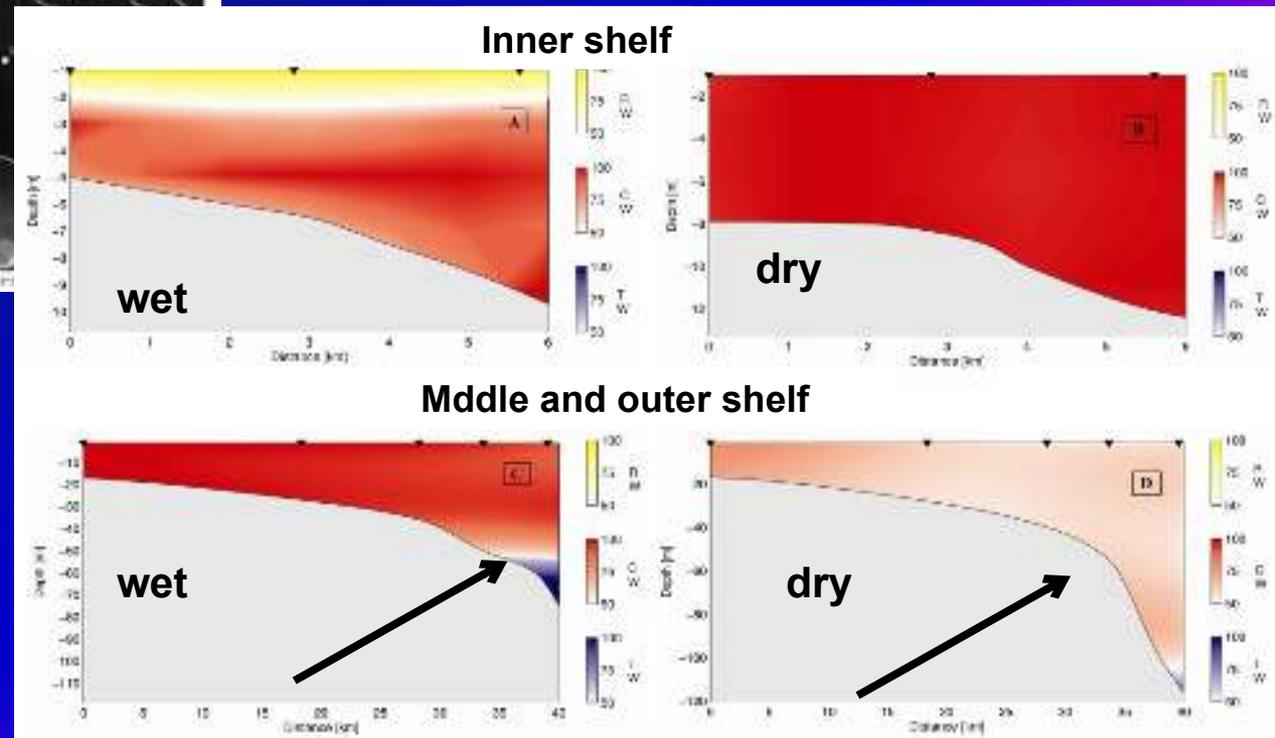
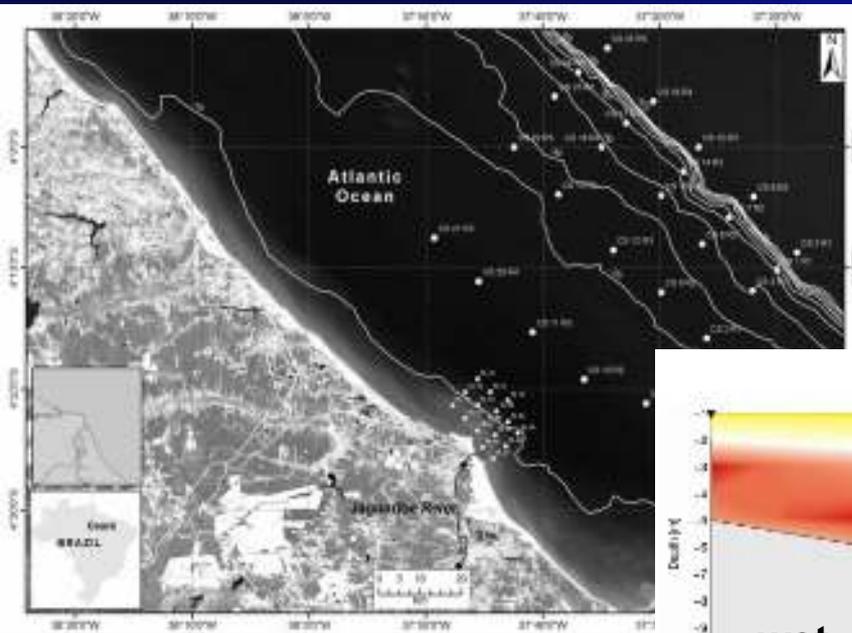
The impact of ocean water on continental shelf off the semi-arid coast of Brazil. Slide & Model, courtesy of Dr. Edmo Campos, USP



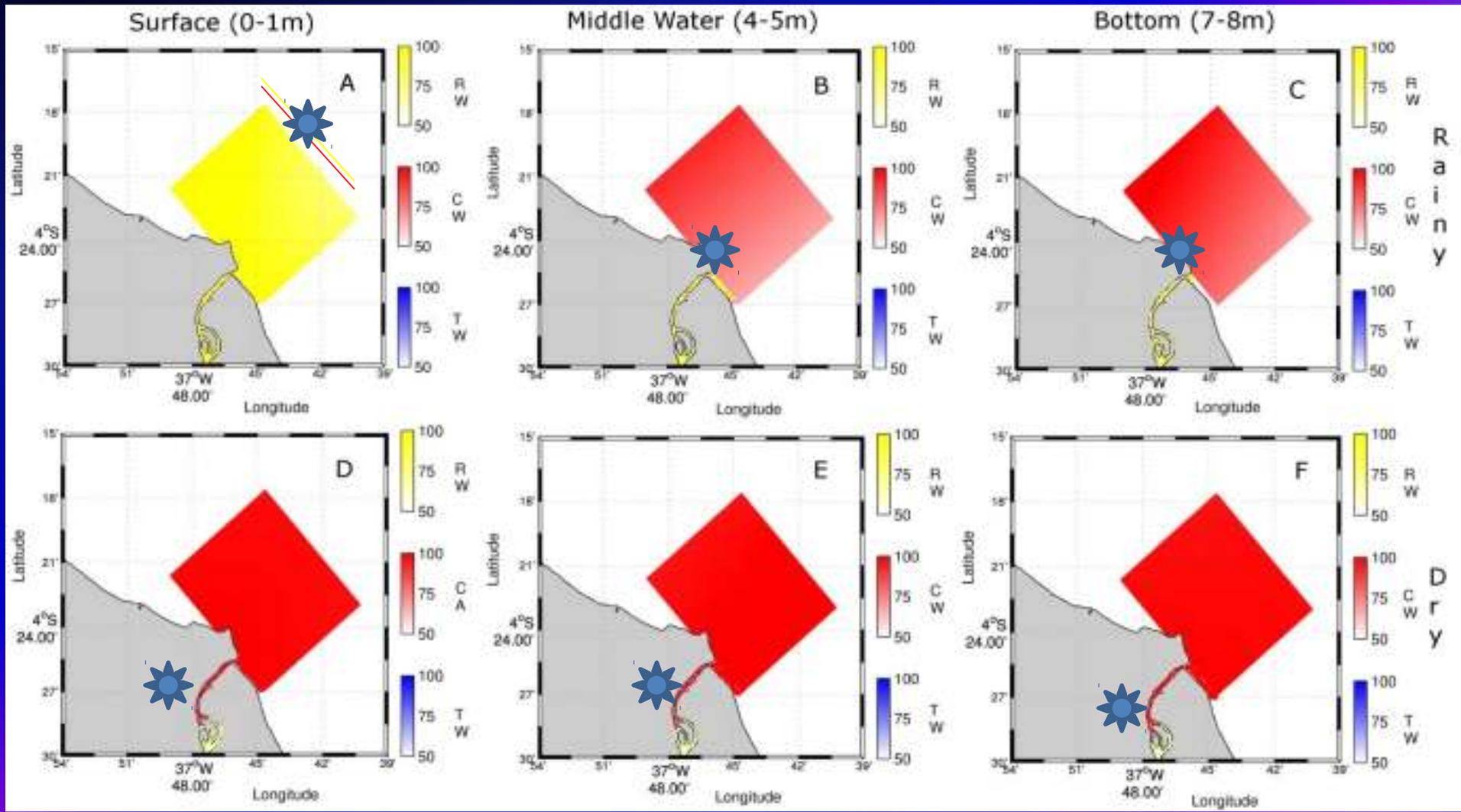
Surface circulation off the Brazilian coast is part of a “Super Gire” connecting the South Atlantic ocean with the Indian Ocean. The South Atlantic is the ocean where highest heat accumulation occurs due to global warming.

Indian Ocean waters “leak” to the South Atlantic, a key element in the global thermohaline circulation. Courtesy Dr. Edmo Campos, USP.

✓ **Temporal and spatial distribution of continental water masses combining multi-tracers analysis and simultaneous sampling grids in river, estuary, plume and continental shelf, show freshwater plume during the rainy season and penetration of Tropical Waters (Oceanic) into the shelf. (↗ (Dias, Castro & Lacerda, 2011)**



Choking the estuary increases water residence time, augmenting reactivity and bioavailability of substances. Stronger ocean forcing moves mixing zone and reactivity processes landward (Dias, Castro & Lacerda, 2011)

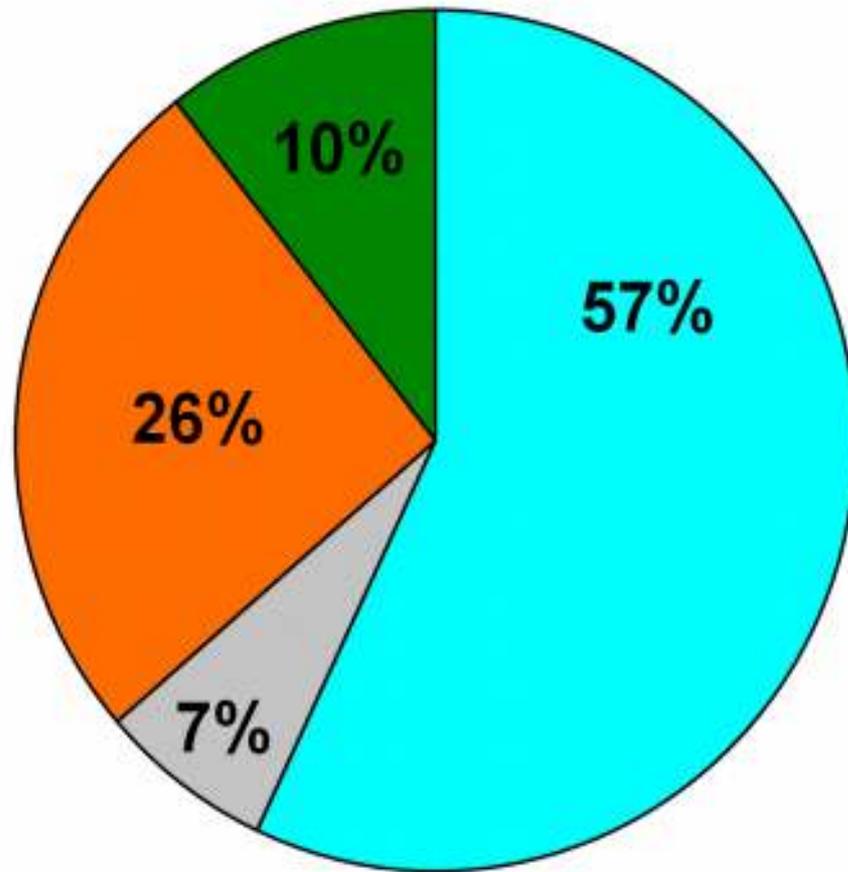
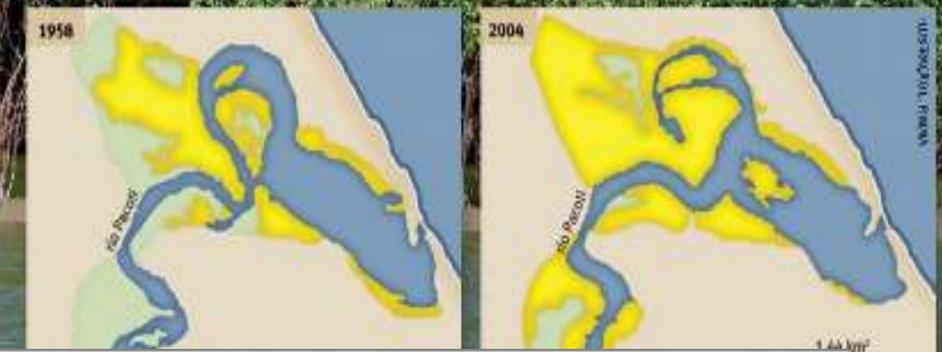


Mixing zone

What are the major impacts of the processes described above on the fate of pollutants?

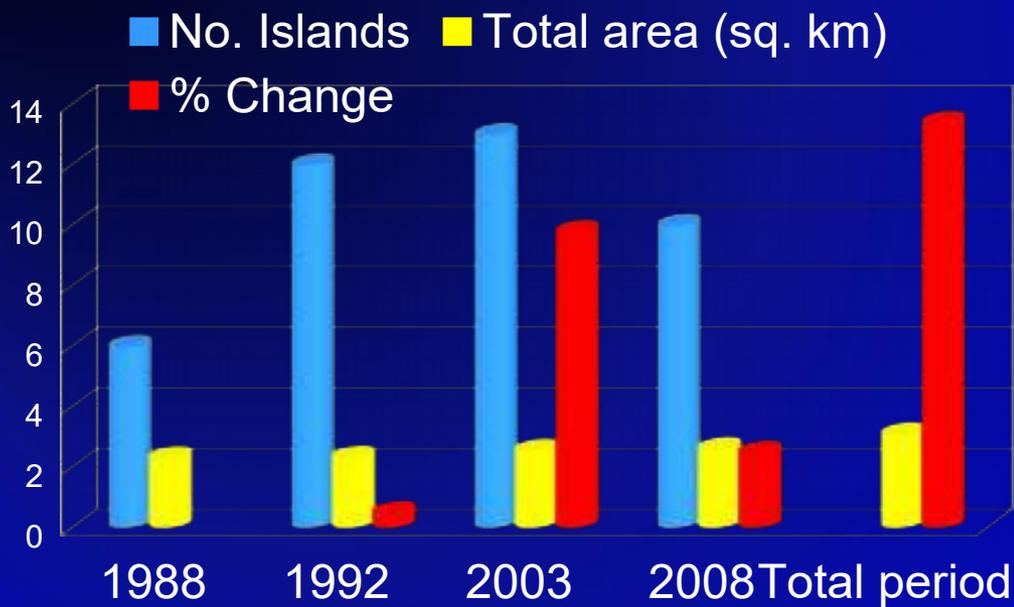
How the chemistry of pollutants responds to the increasing choking of estuaries and decreasing continental runoff, sedimentation in estuaries, mangrove expansion and longer water residence time there?

Origins of alterations identified in 41 estuaries of the semiarid littoral of NE Brazil. Comparing radar data from 1980 to Landsat, SPOT & Quickbird data from 1999 to 2013



?

Changes in island area in the Jaguaribe River estuary between 1988 and 2008 (Godoy & Lacerda, 2013)



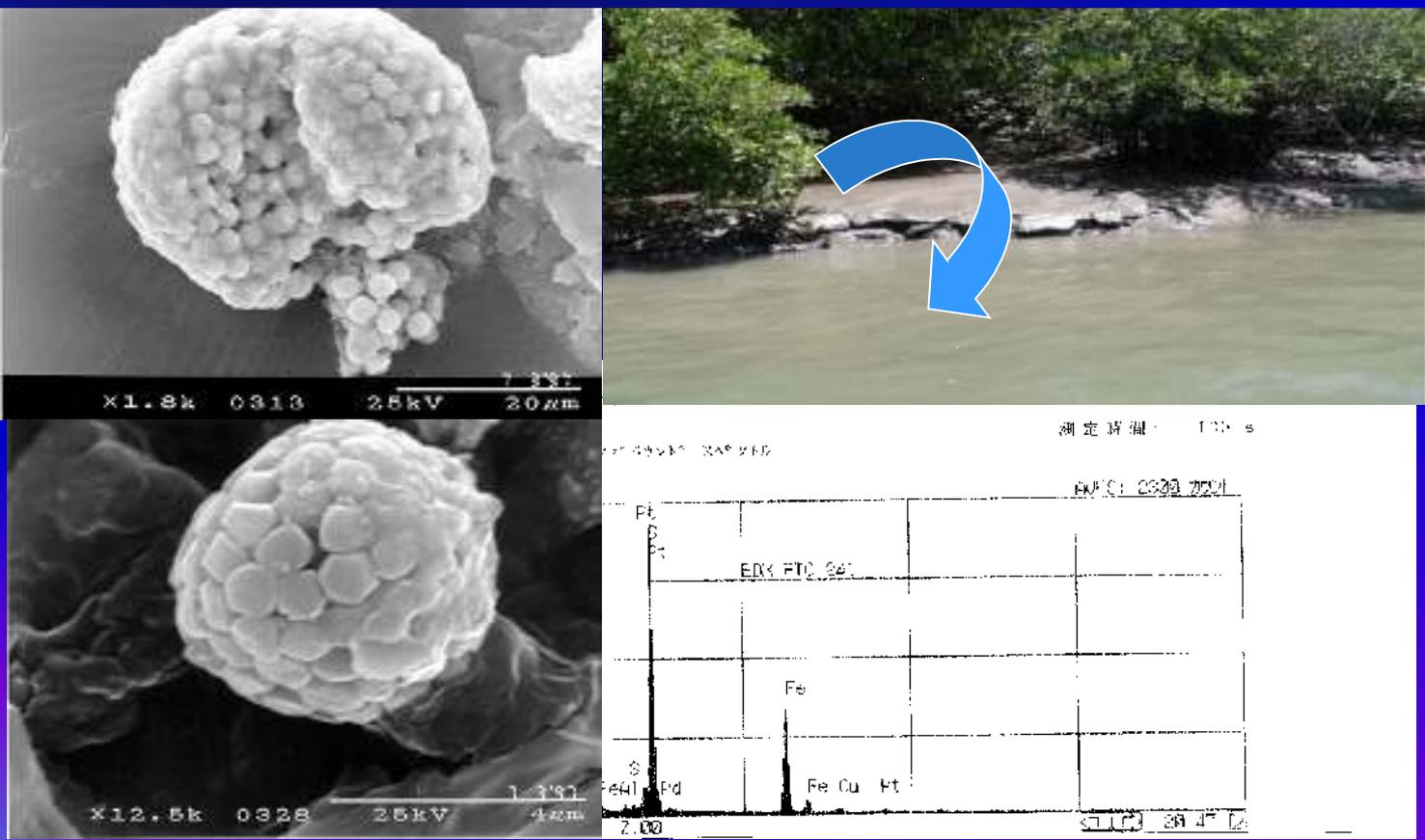
Mangrove expansion in NE Brazil (Maia, Gentil & Lacerda, 2006)

Parameter	km	%
Total mangrove area in 1978	278	
Total mangrove area in 2004	352	
Increase (uncertainty)	74	21% (3%)

Three generations of mangroves along the Jaguaribe River, NE Brazil

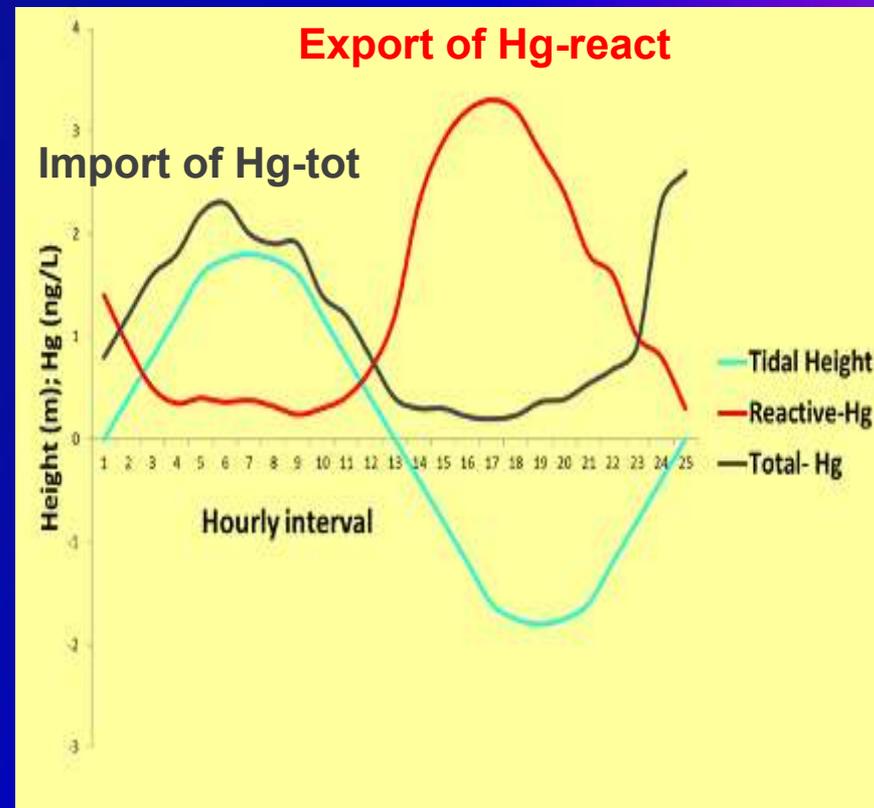
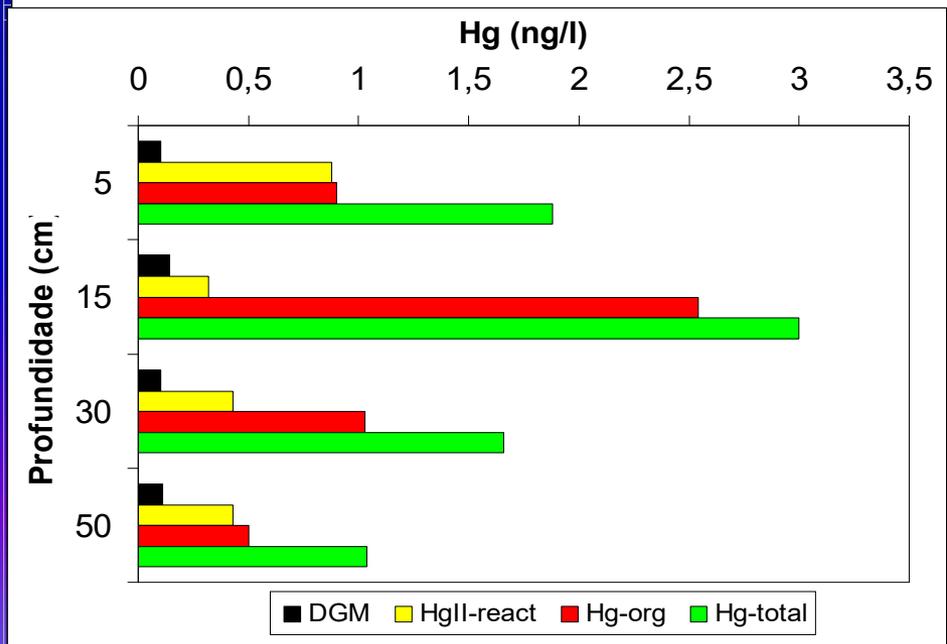
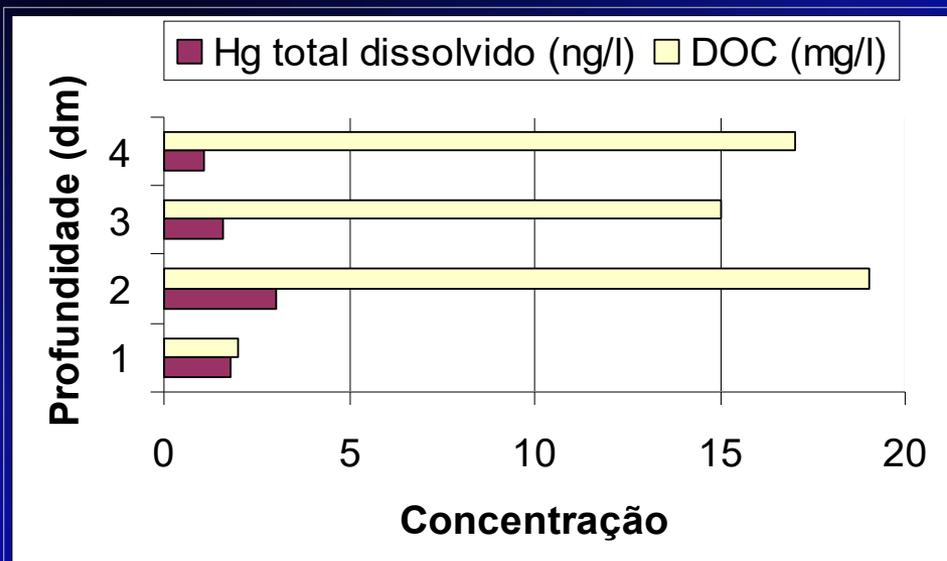
Biogeochemical Scenario

- ✓ Augmenting water residence time and sedimentation at the estuary increases mangrove areas and its metabolism based on dissimilatory sulfate reduction expands to larger areas.
- ✓ There is a larger export of DOC from the incomplete respiration of organic matter by anaerobes.
- ✓ Deposited metals from continental origin accumulate and suffer chemical changes instead of rapid being exported to the continental shelf.



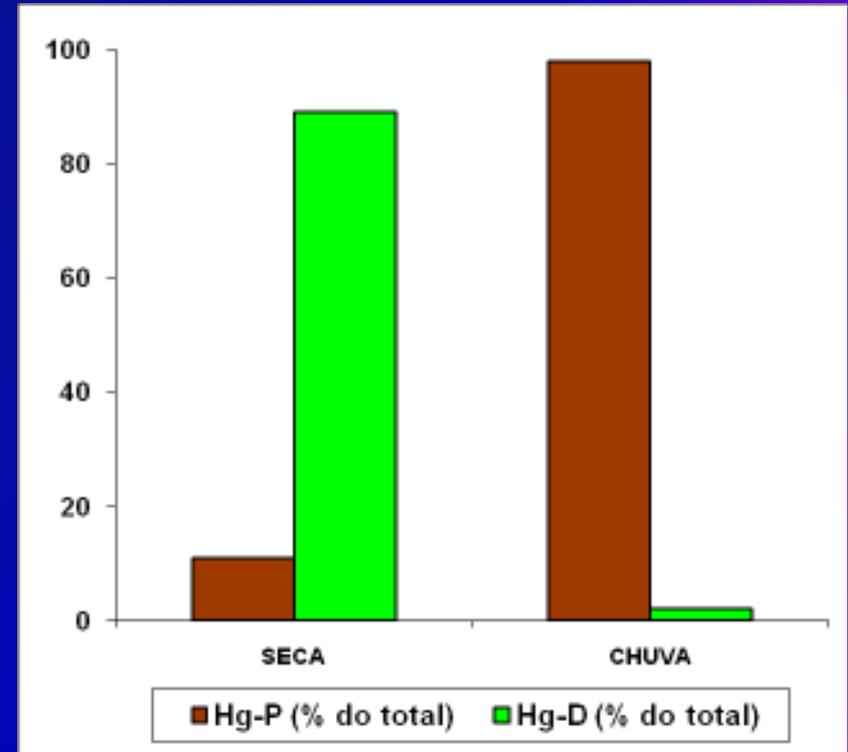
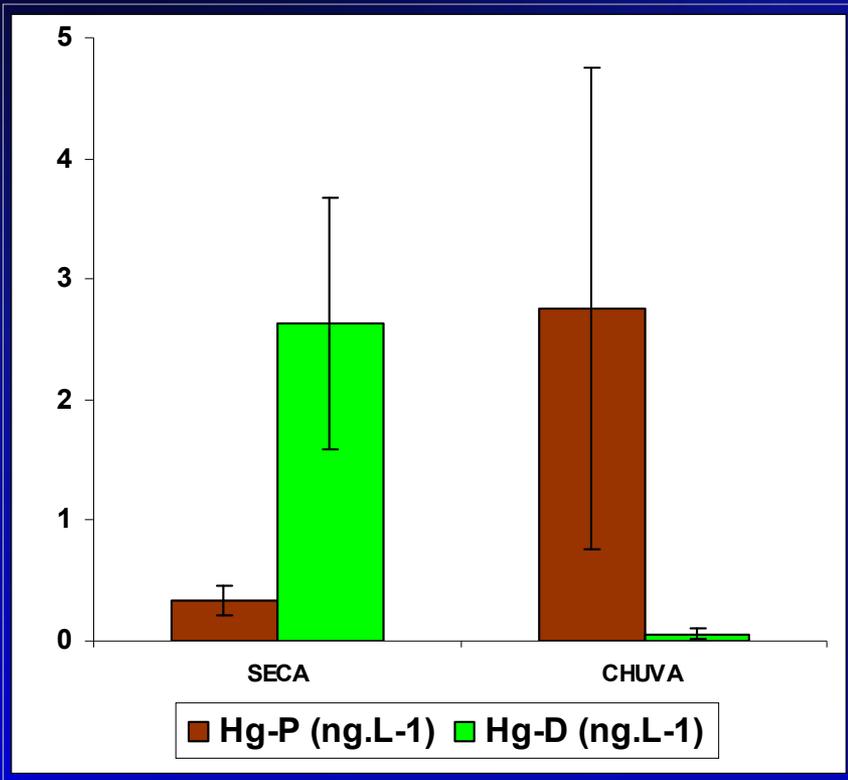
Pires & Lacerda (1997)
Lacerda (1998)
Lacerda (2007)

Organic-Hg complexes production in porewater facilitates Hg export from sediments



Tidal export of Hg from the from a mangrove forest (Lacerda et al., 2001)

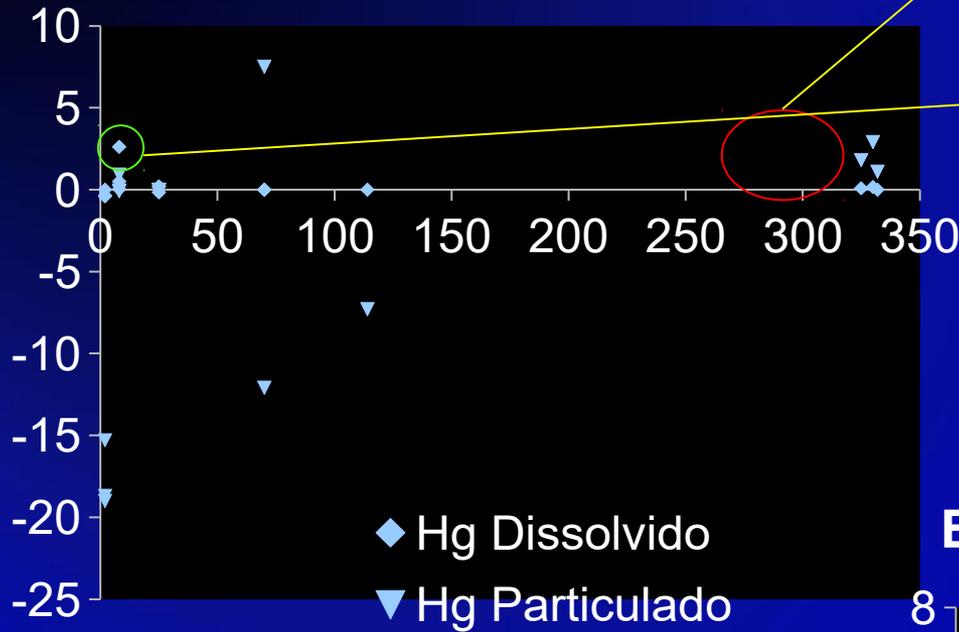
Relative Speciation of Hg in the dry and wet season at the Jaguaribe Estuary (Lacerda et al., 2013)



Dissolved Hg species dominate the flux during the dry season.

Particulate Hg species dominate the flux during the wet season.

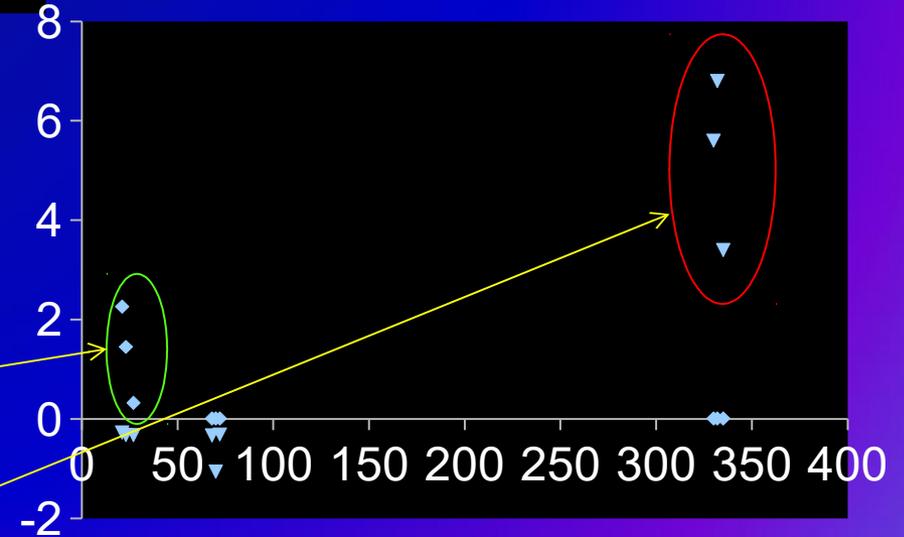
River to estuary



Export of particulate Hg from river to estuary occurs only under **intermediate and high fluvial fluxes**; Dissolved Hg export occurs with **fluvial fluxes close to zero**

Rain vs Transport

Estuary to Sea

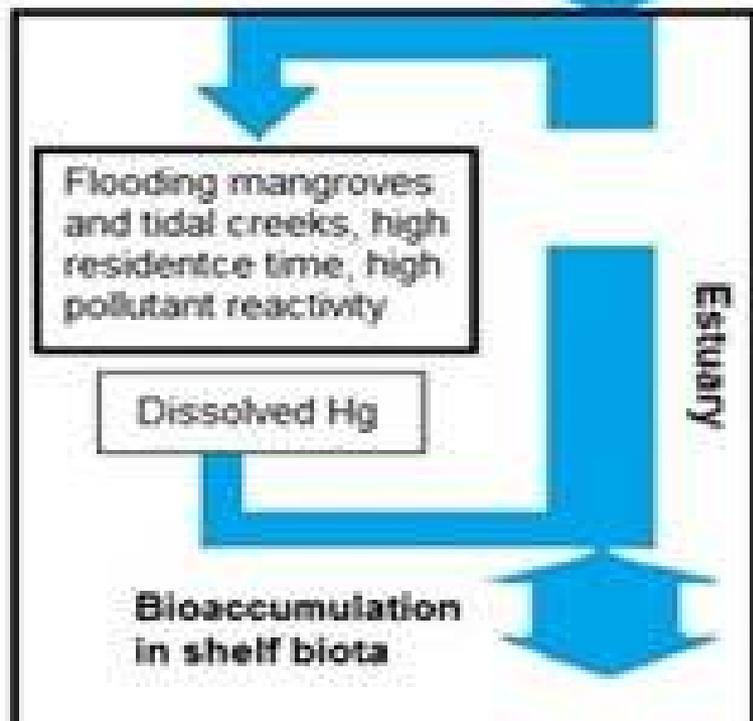


Export of dissolved Hg occurs only during the dry season **with discharge close to zero**. Particulate Hg export occurs only under **very high water discharge**

Dry season
(7-8 months)

river

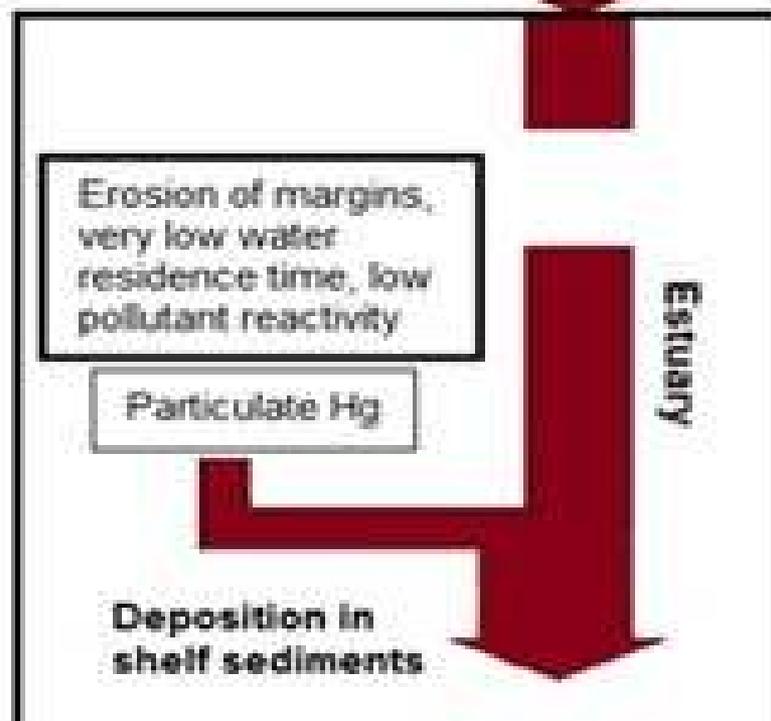
low flow



Wet season
(4-5 months)

river

high flow



Southwestern Atlantic Ocean

Mechanisms involved in the augment of Hg dissolved species (bioavailable), favored by the augment of the water residence time within the estuary

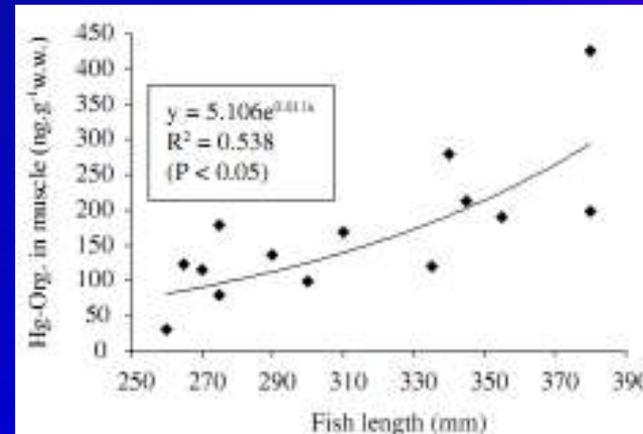
- ❖ **Desorption of Hg from suspended particles due to salinity increase and saline intrusion landward**
- ❖ **Export of pore waters enriched in DOC from ever larger mangrove forests**
- ❖ **Formation and export of soluble Hg-organic complexes**
- ❖ **Increased uptake by the phytoplankton associated with higher water transparency.**
- ❖ **Faster assimilation and accumulation in the food chain**

Augment of water mass chocking and water residence time in estuaries. Increasing saline intrusion and accumulation of continental materials inside the estuary

Continental fluxes may decrease in total but qualitative changes occur due to longer residence time augmenting reactive and bioavailable species (e.g. Hg)

Increasing reactive species increases biological uptake, food chain transfer and human exposure.

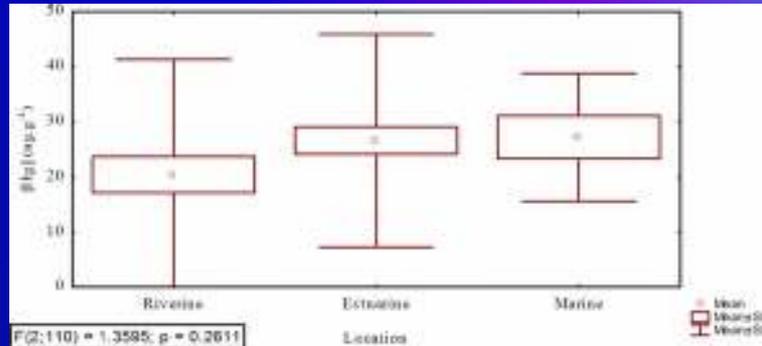
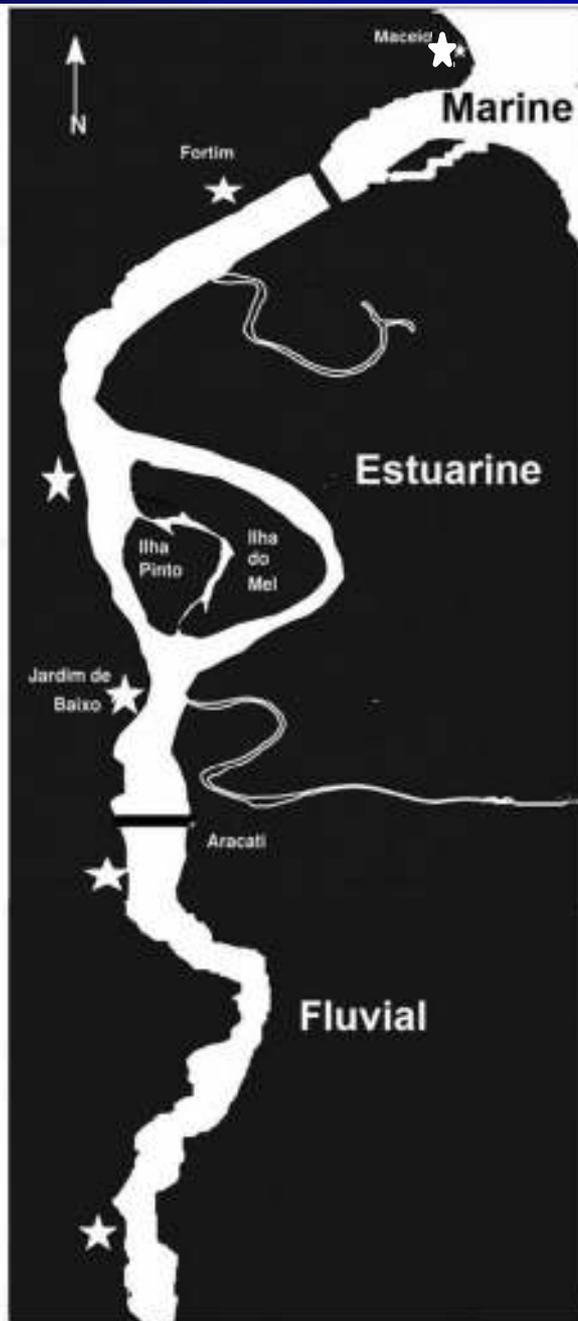
Hg-Org



Hg em *Cephalopholis fulva* do mar cearense (Lacerda et al., 2006)

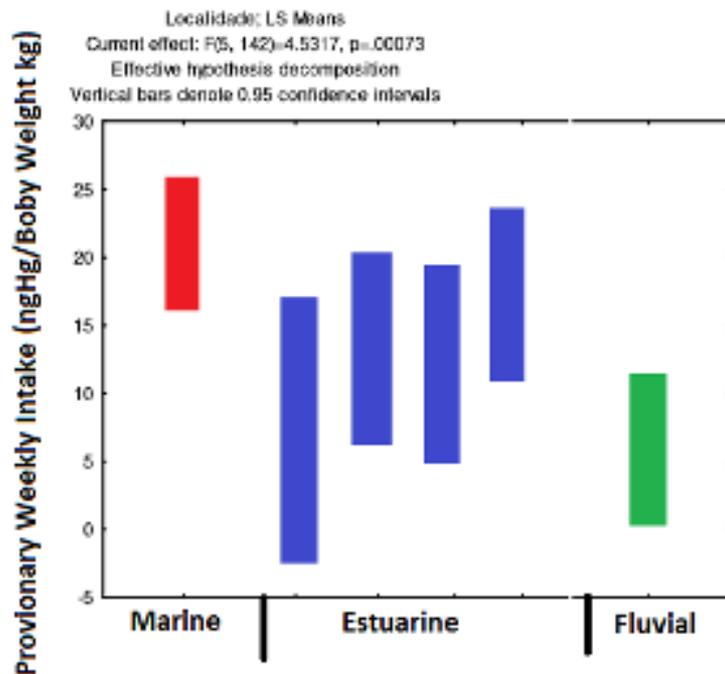


★ Sampled villages



Hg in Fish

Human exposure



Obrigado!

<http://inct.cnpq.br/web/inct-tmcocean/home/>

CNPq - INCT - TMCOcean



**INSTITUTO NACIONAL DE CIÊNCIA E TECNOLOGIA
DE TRANSFERÊNCIA DE MATERIAIS CONTINENTE-OCEANO**

INSTITUTO DO MILÊNIO

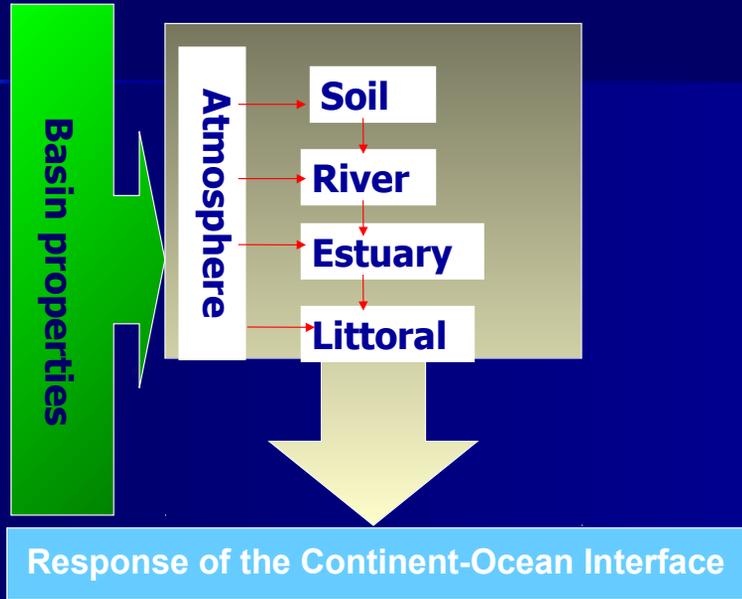
CNPq



Continent-Ocean Transfer Processes *

(Concepcion at the end of the 20th century)

Biogeochemistry of transfer processes

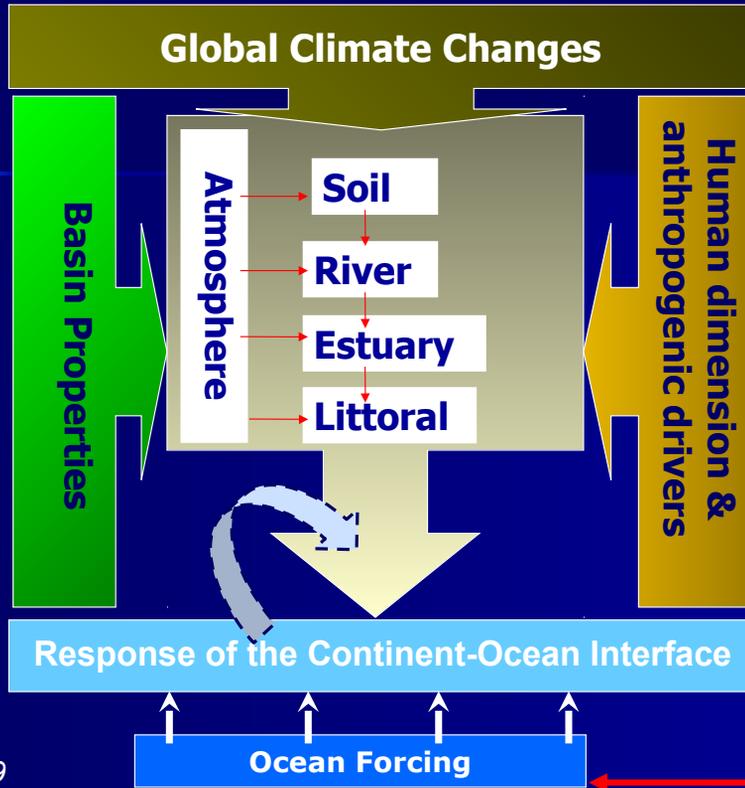


Lacerda, 2009

*Most legislation still based on it!

Present -day Continent-Ocean Transfer Processes *

Biogeochemistry of transfer processes



Lacerda, 2009

Principals characteristics of the COI

-  **1** – Transfer of water, mass and energy occur through the continent-ocean interface at large spatial scale both in terrestrial and marine adjacent areas
-  **2** - Transfer occurs simultaneously both at continent-ocean and ocean-continent directions at different temporal e spatial scales.
-  **3** – Transfer is affected by natural and anthropogenic vectors.

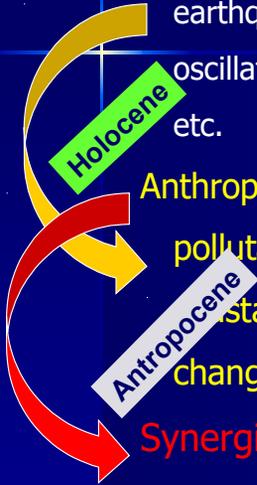
c.f. Kjerfve, 2007

Vectors affecting the continent-ocean transport

Naturals: geotectonic (subsidence/elevation), wind, earthquakes, hurricanes, tsunamis, inundations, sea level oscillation, type and abundance of coastal vegetation, etc.

Anthropogenic: wastewaters, agriculture runoff, pollutant emissions and remobilization, conversion of coastal areas, engineering works, global climate changes.

Synergies: vectors act simultaneously and do affect each other, including through feedback mechanisms, in generally very poorly known.



Major effects of anthropogenic vectors

- (i) *Human activities largely accelerate biogeochemical cycles and the transfer of materials at the planetary levels;*
- (ii) *Natural fluvial filters have been constantly altered, particularly by the construction of dams and deforestation of gallery forests and conversion of coastal vegetation;*
- (iii) *Fluvial discharges to the oceans are presently artificially controlled and reduced by engineering interventions (dams, diversion withdraw) and due to global climate change, at least in lower latitudes).*

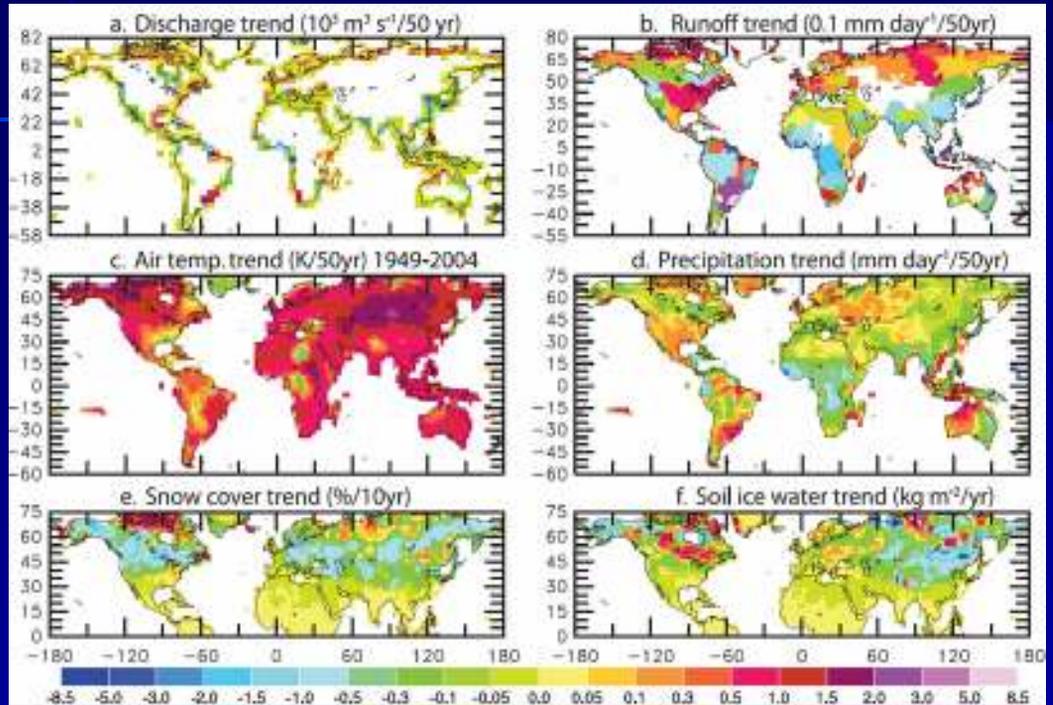
Meybeck a & Vörösmarty (2005)

Principals classes of anthropogenic vectors affecting the transport of materials at the continent-ocean interface

Vectors	Pressure	Impact
Agribusiness/ Aquaculture	Increasing loads of sediments, nutrients and contaminants, permeability of surfaces, decreasing water availability	Sedimentation Eutrophication
Urbanization / Industrialization		Sedimentation Eutrophication Contamination
Dams	Retention of sediments and nutrients Regularization of the fluvial flux	Sedimentation Erosion Oligotrophy
Global climate change	Sea level rise, alteration of the rainfall regime	Sedimentation Erosion

Marins et al. (2002)

Global changes augment continental runoff in high latitudes, and decrease in lower latitudes and in semiarid regions in particular (Dai et al., 2009).

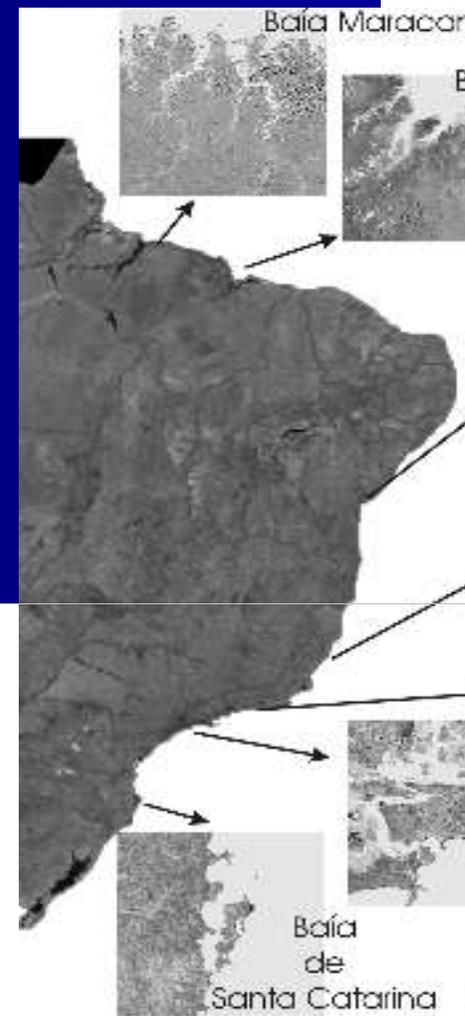
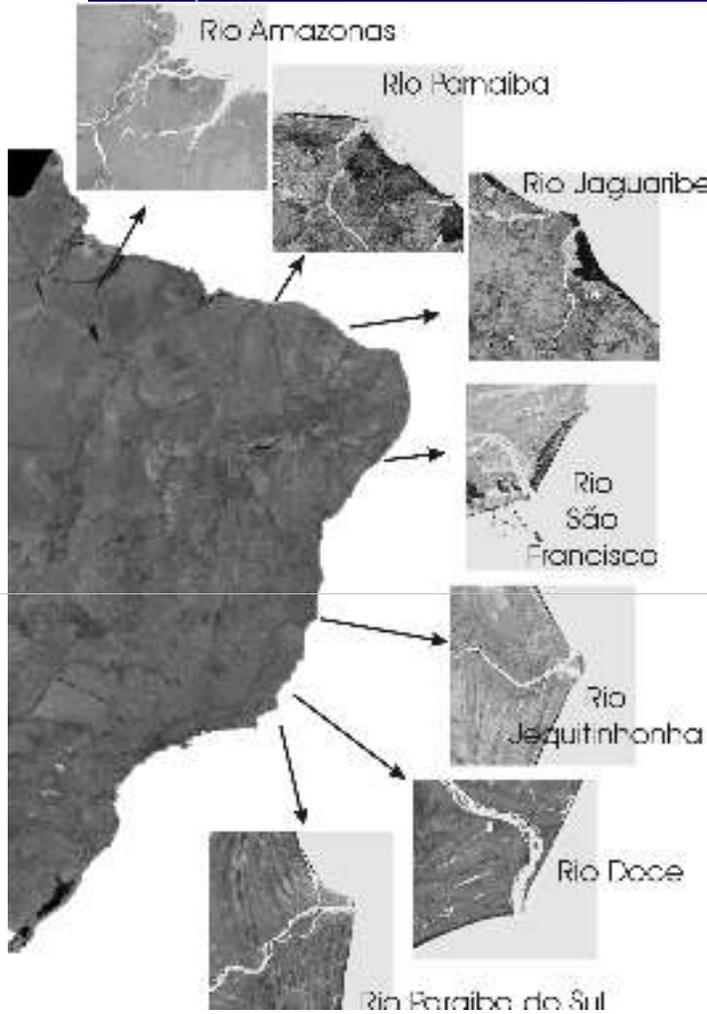


Classes of interface systems in Brazil (Knoppers *et al.*, 2009).

1. Spatial Scale

Exporters / Accumulators

Accumulators/ Exporters



Typical exporting systems form fluvial plumes over continental shelves, but may display seasonality



1. Spatial scale

Descarga de sedimentos pelo Rio J

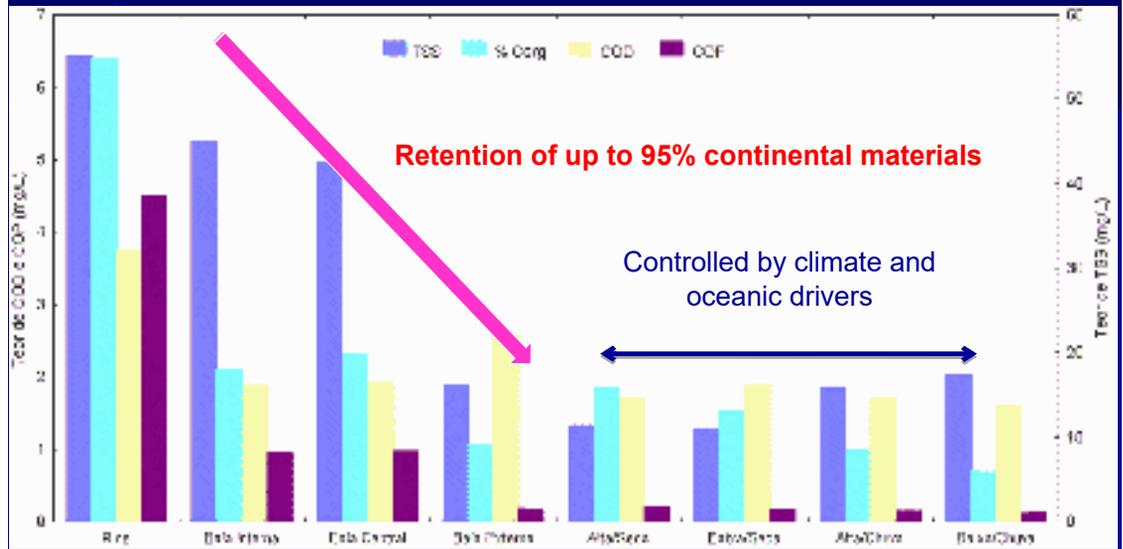


Typical retainer systems forms
sedimentary environments in the estuarine
zone

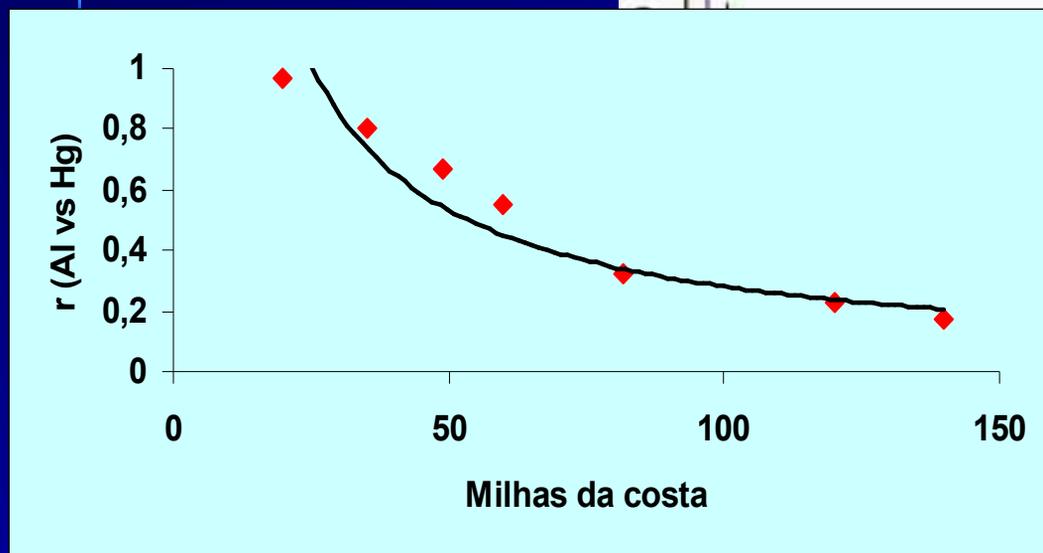


1. Spatial scale

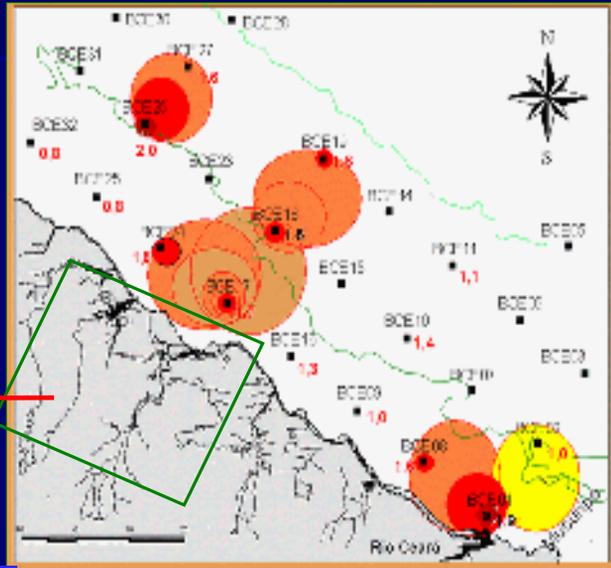
Concentration changes of COD, COP e TSS along Sepetiba Bay, SE Brazil



Hg vs Al in sediments along the continental shelf in SE Brazil



Al distribution in shelf sediments from NE Brazil

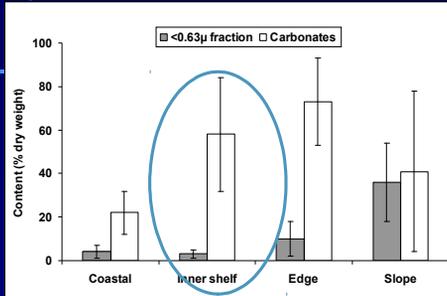


Irrigated perimeter

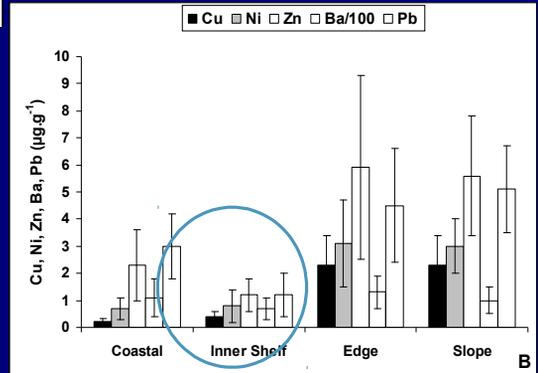
1. Spatial scale

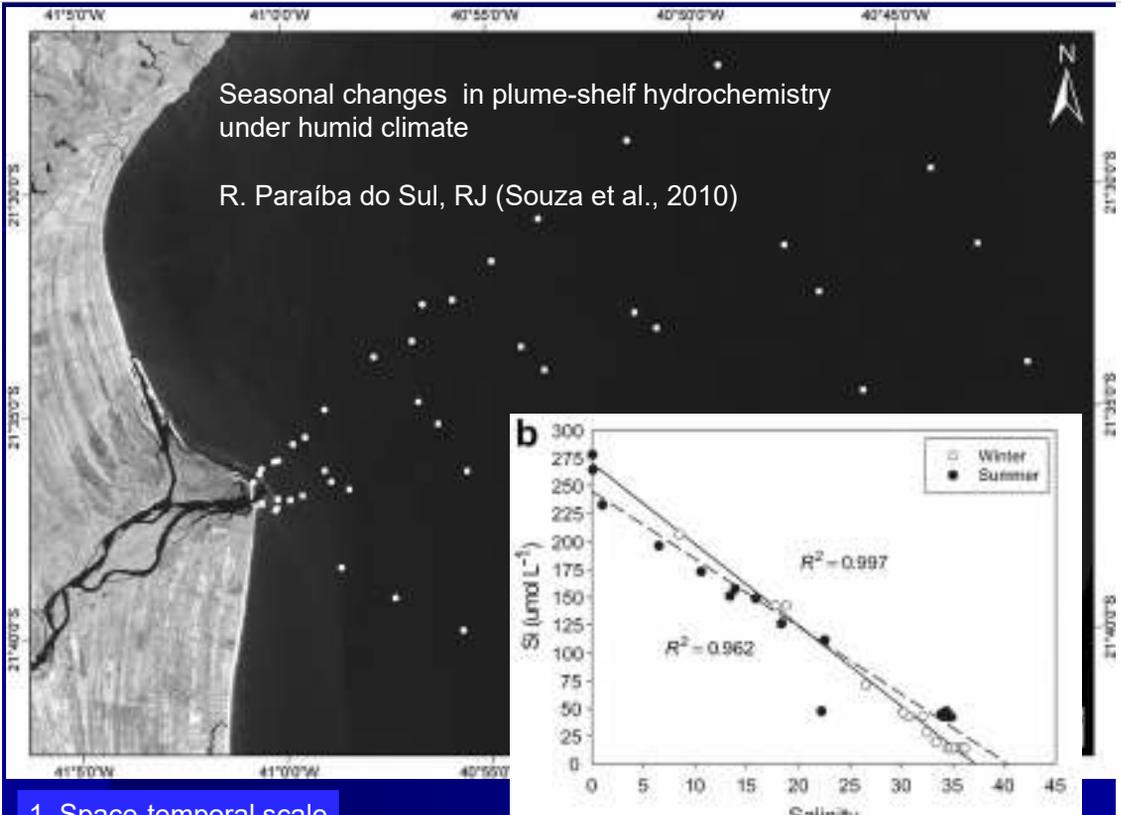
Trace metals in shelf sediments in an offshore oil and gas exploration area in NE Brazil (Lacerda et al., 2013)

Potiguar Basin, RN

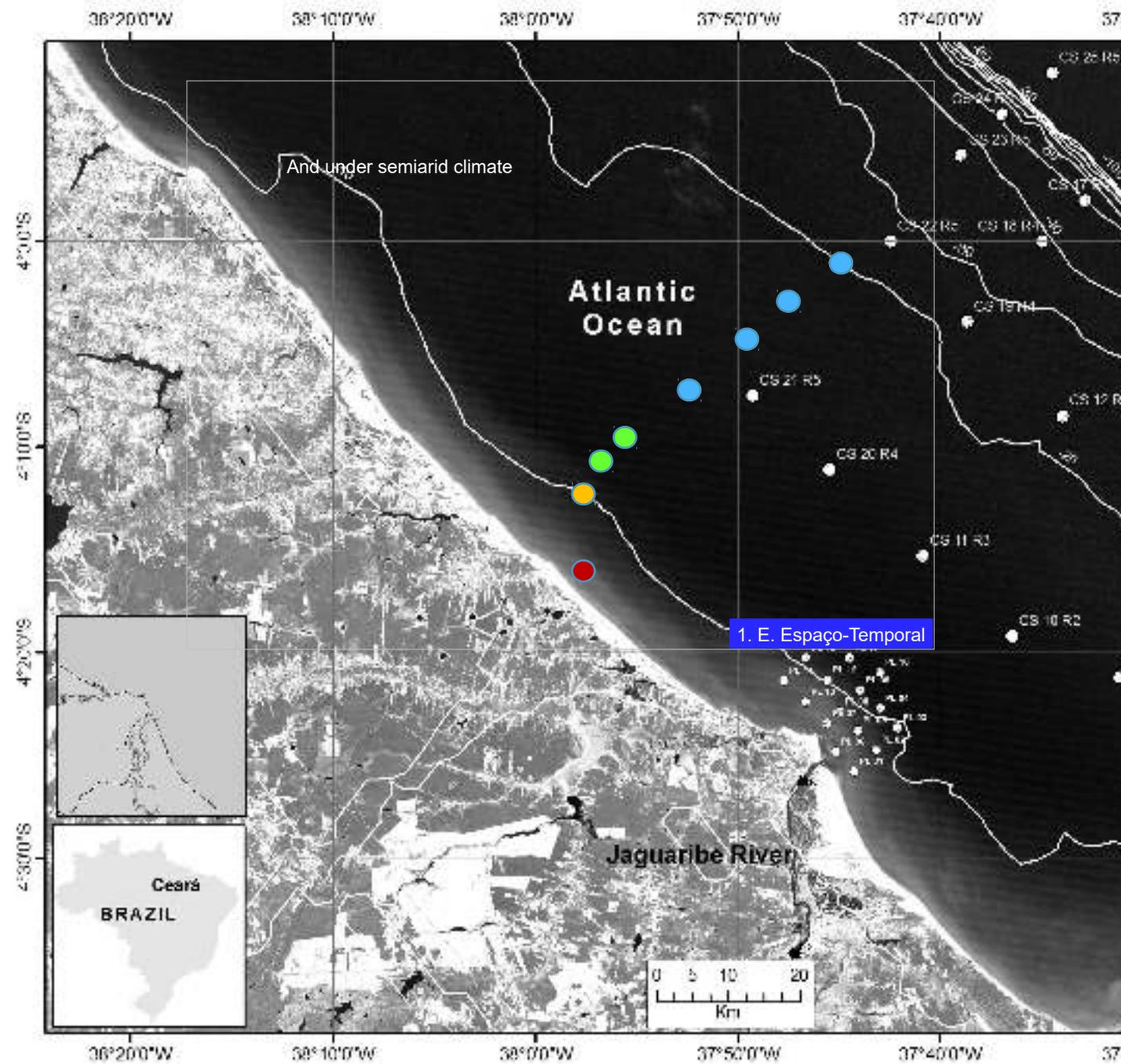


1. Spatial scale





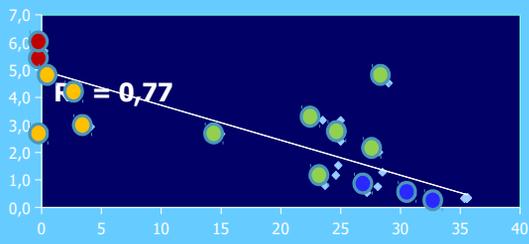
1. Space-temporal scale



Seasonality under semiarid climate

R. Jaguaribe, CE (Lacerda et al., 2010)

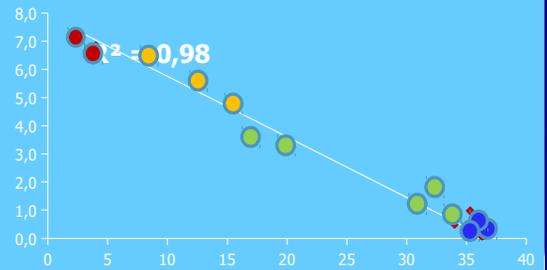
Si vs Salinidade, Período Chuvoso

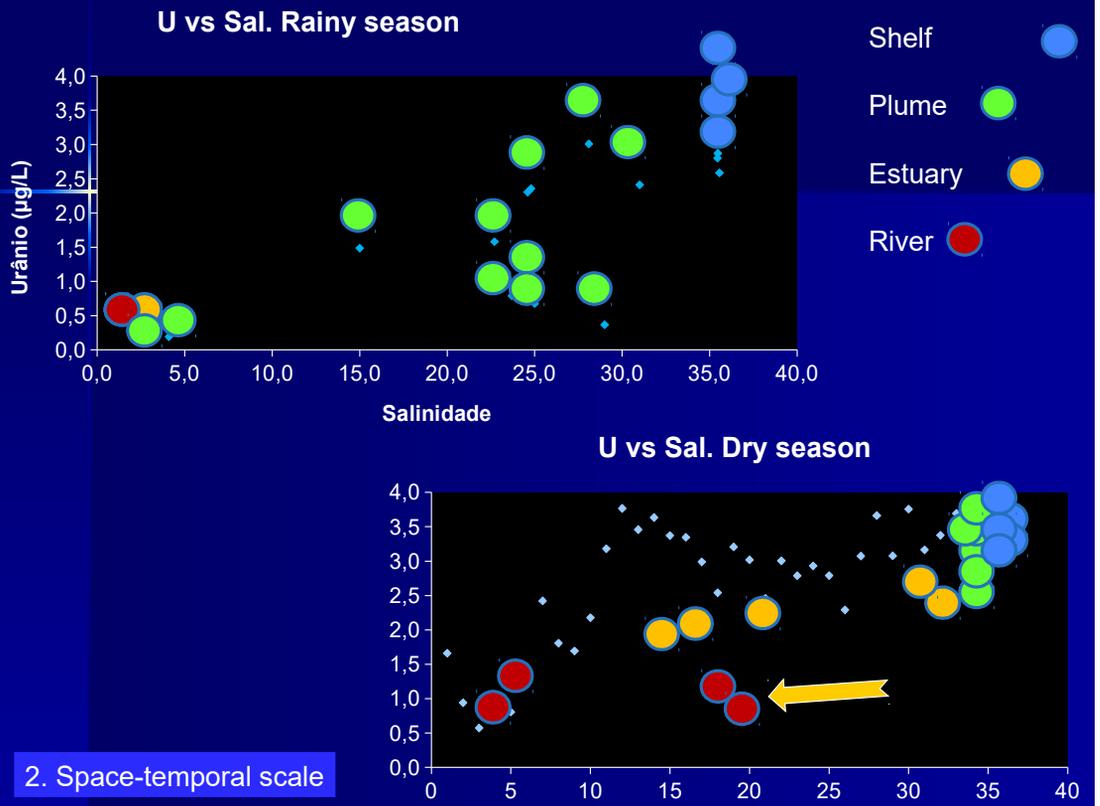


- Shelf 
- Plume 
- Estuary 
- River 

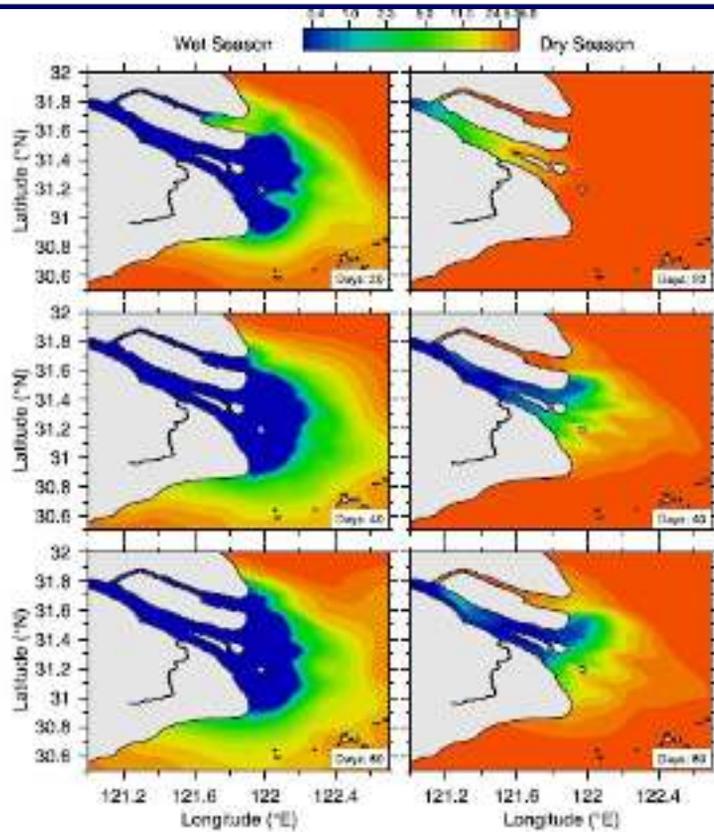
1. Space-temporal scale

Si vs Salinidade, Estação Seca





2. Space-temporal scale



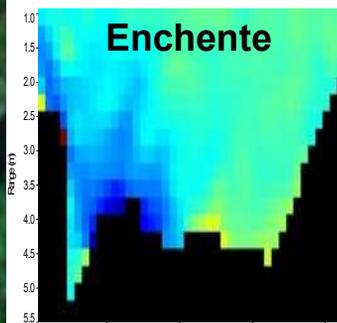
Salt intrusion at
the Yangtze,
China
c.f. LOICZ
(2010)

Fluxes (ADCP) under umid climate

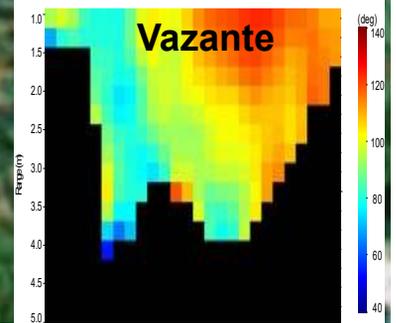
Rio de Contas, Itacaré, BA

2. Space-temporal scale

Contour Variable: Velocity - Direction



Contour Variable: Velocity - Direction

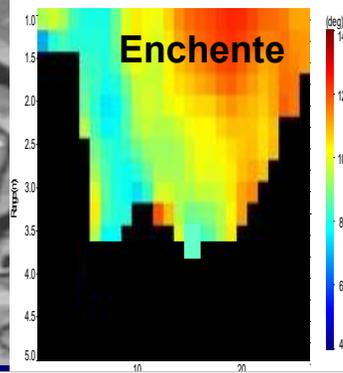


Fluxes under
semiarid climate
(ADCP)

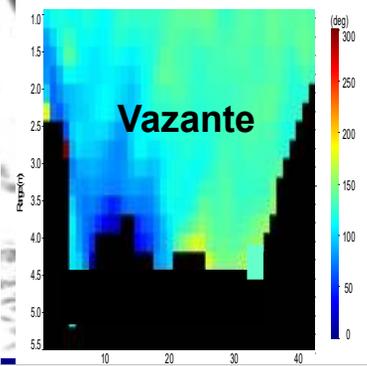
Rio Jaguaribe,
Fortim, CE

2. Space-temporal

Contour Variable: Velocity - Direction



Contour Variable: Velocity - Direction



Globally, about 40% of transported materials from continental origin by rivers are trapped in estuarine and deltaic sediments.

Materials passing through the estuarine-deltaic filter are deposited in the continental shelf according to shelf characteristics.

Less than 10% is eventually exported to the deep ocean

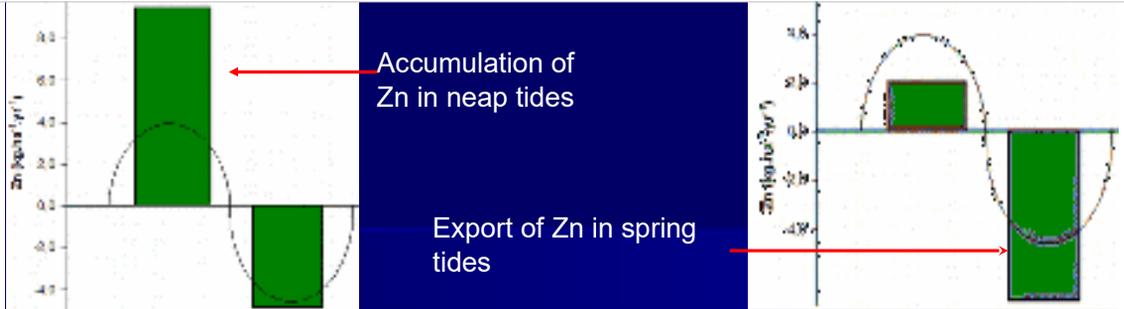


Post-depositional colonization of estuarine and deltaic sediments by plants changes the biogeochemical nature of the environment

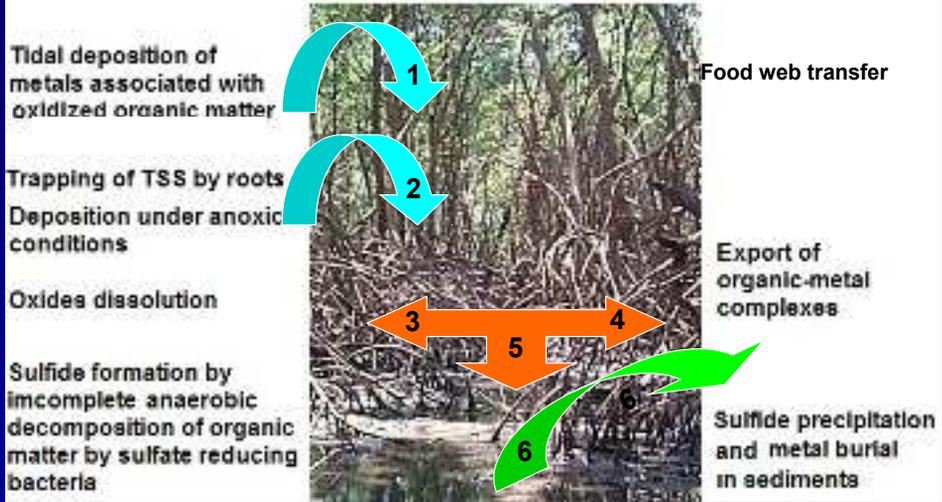


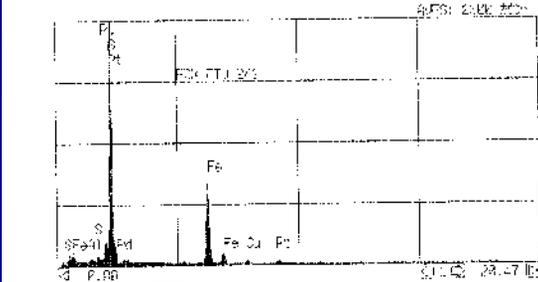
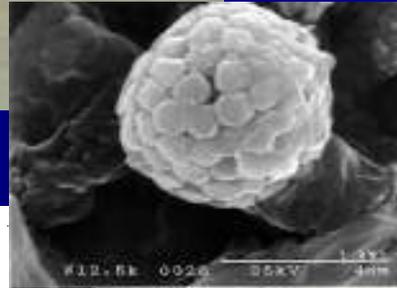
e.g. Impact from mangrove colonization of
significance to estuarine ecology and sustainable use

- Augment of the deposition of fine sediments and sedimentation rates
- Decreasing aeration of sediments
- Increasing organic matter deposition and preservation in sediments
- Increasing consumption of dissolved oxygen
- Anoxia & sulfate reduction



Lacerda (1998)

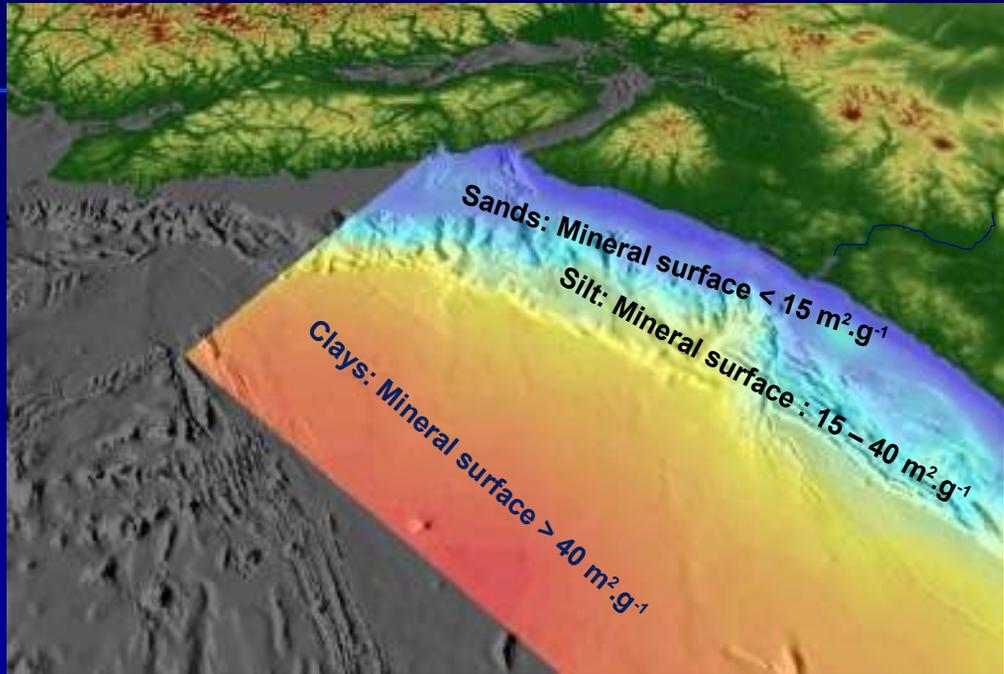


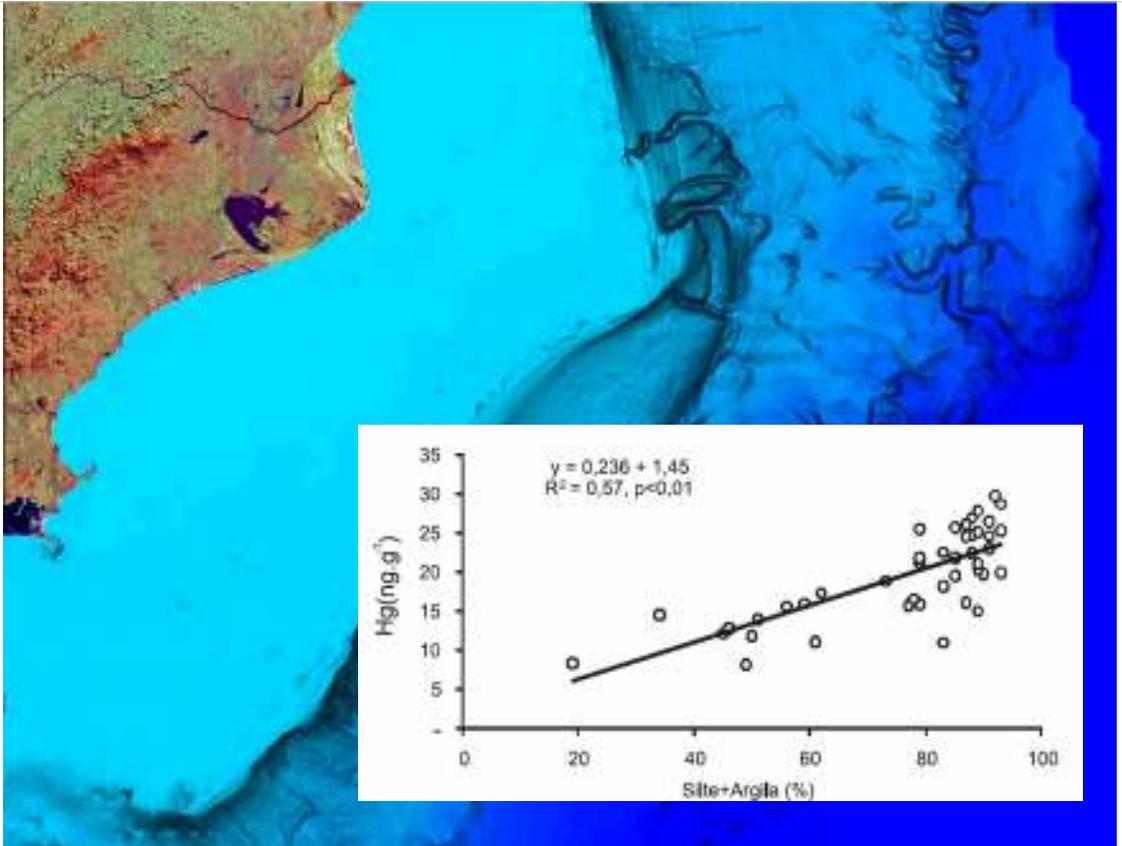


Framboids of pyrites that release metals upon oxidation due to erosion and sea level rise or decreasing fluvial sediment transport

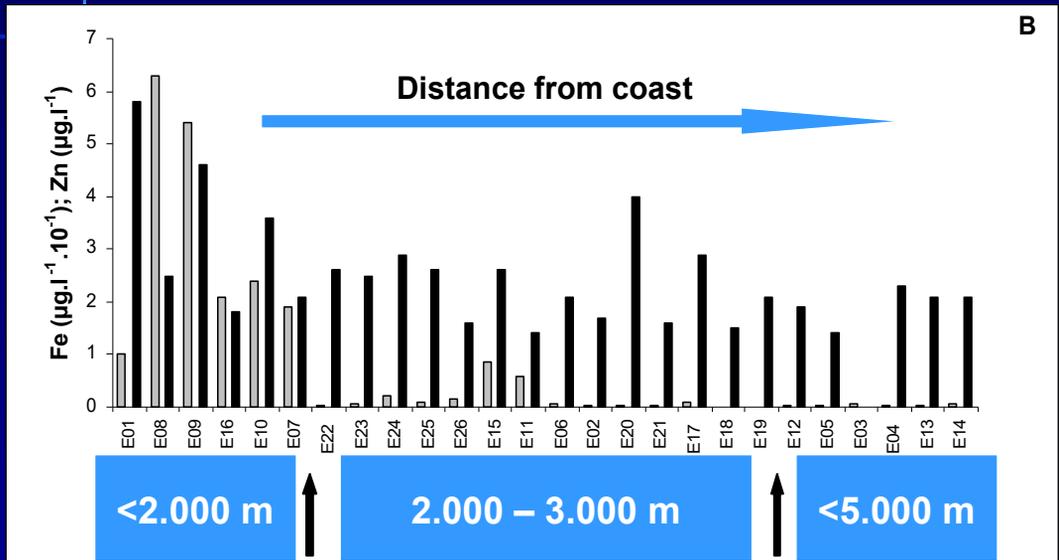
Pires & Lacerda (2007)

Typical granulometry of shelf sediments



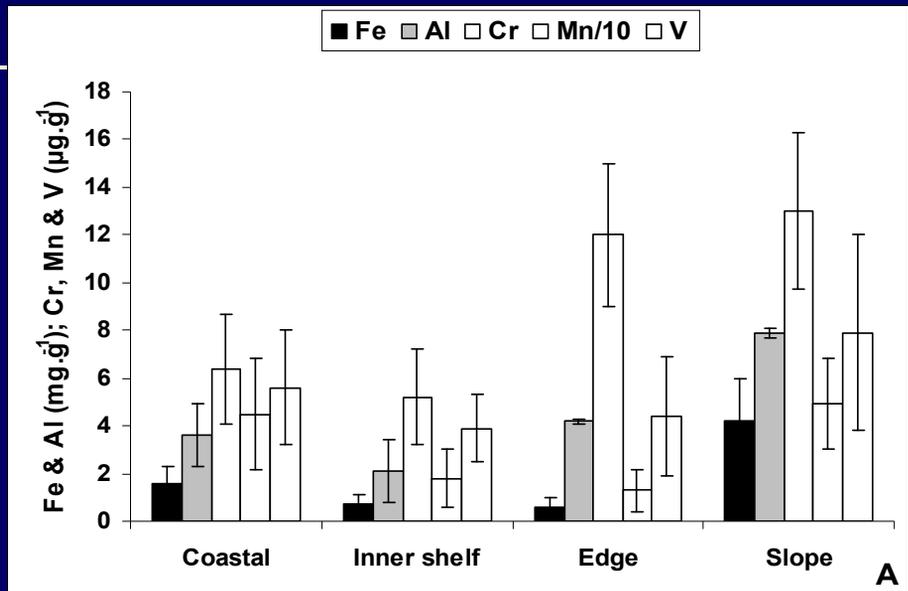


Metal distribution in NE Brazil shelf sediments



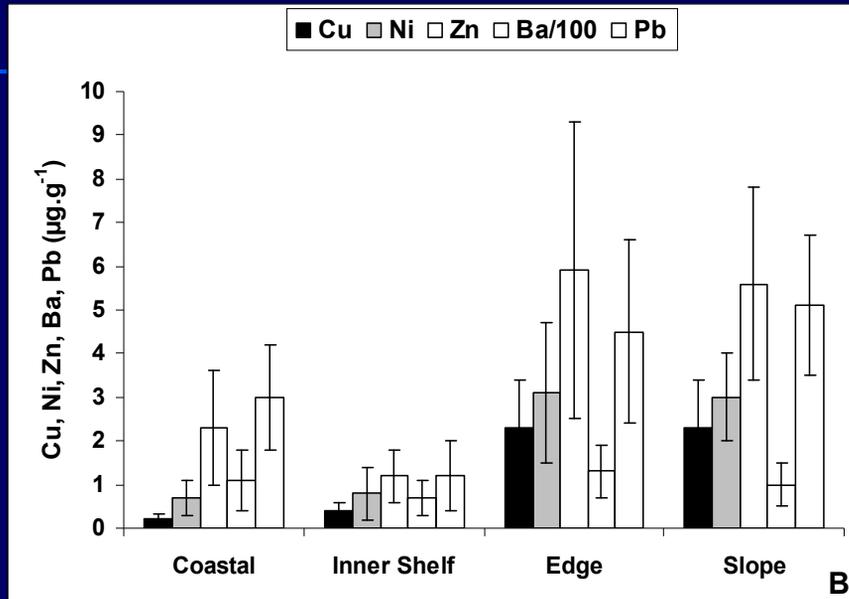
Influence of continental sources

Metal distribution in NE Brazil shelf sediments



Influenced by marine processes

Metal distribution in NE Brazil shelf sediments

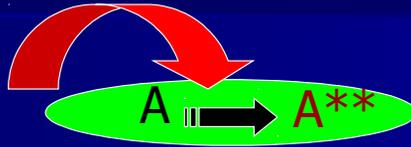


Influenced by marine processes

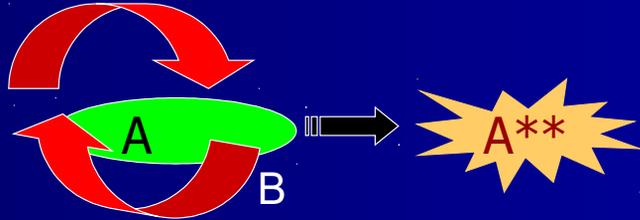
“The magnitude of transfer processes are today controlled mostly by anthropogenic drives”.

Forms of action

1
Vectors causing direct changes on the biogeochemical properties of the environment through emission of alien substances (mostly typical of the last century)



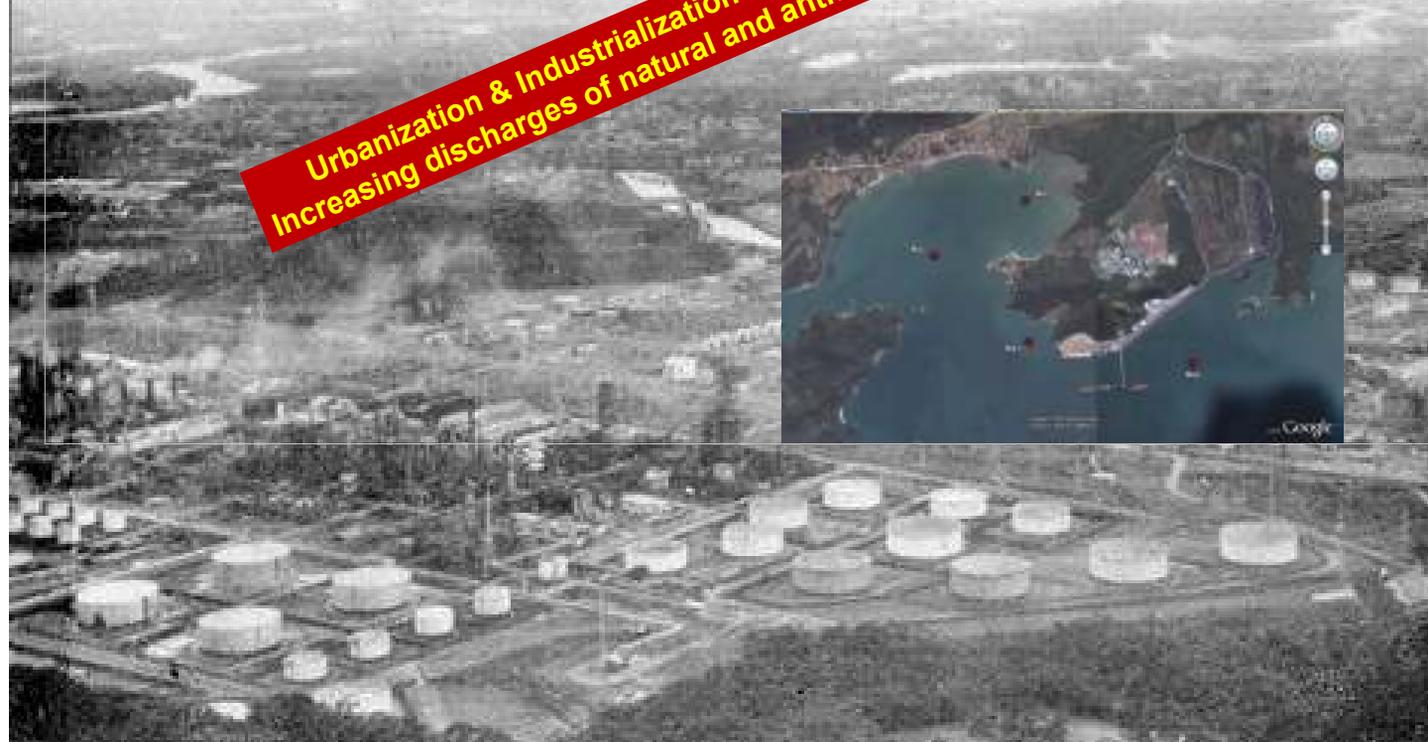
2
Vectors causing direct changes on the biogeochemical properties of the environment through interactions with its properties or among themselves (our challenger today).



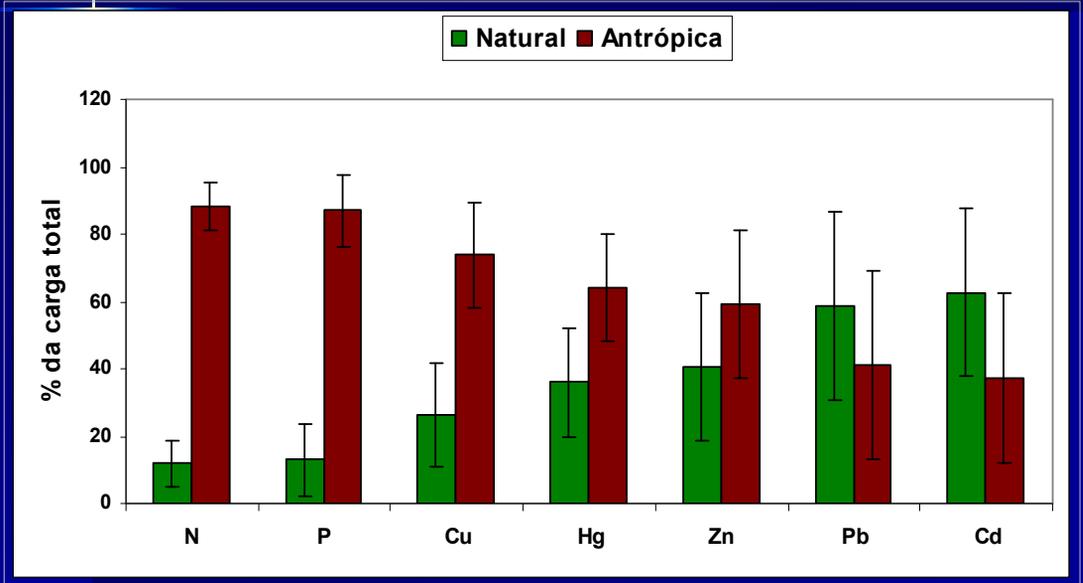


LA MENTIGLIANADA BAVADA SANTISTA - AGEM

**Urbanization & Industrialization & Agriculture/Husbandry
Increasing discharges of natural and anthropogenic substances**



Relative importance of natural and anthropogenic sources of nutrients and metals to the NE Coast of Brazil. Average values from 19 estuaries.



Sources	Emission factors		Substances present in effluent		
	N and P (t/km ² /year); Cu, Hg and Zn (kg/km ² /year)				
Natural sources	N = 0.05 – 0.9 P = 0.01 – 0.06	Cu = 2.0 – 2.6 Zn = 5.0 – 6.5 Hg = <0.001	Mostly associated with particulate matter		Receiving body
Agriculture	N = 0.05 – 2.65 P = 0.12 – 0.56	Cu = 0.7 – 13.5 Zn = 0.04 – 0.13 Hg = 0.02	Nitrate; Ammonia; Phosphate	Cu ²⁺ , Zn ²⁺ , Particulate- Cu and Zn	Soil
Husbandry	N = 0.09 – 1.31 P = 0.09 – 1.73	Cu = 0.3 – 1.0 Zn = 0.4 – 7.3 Hg = <0.001	Ammonia; Phosphate	Particulate- Cu and Zn	Soil
Urban waste waters and runoff	N = 0.03 – 0.55 P = 0.01 – 0.14	Cu = 0.1 – 15.3 Zn = 0.01 – 47.2 Hg = < 0.001	Nitrate; Ammonia; Phosphate; Particulate-P	Cu ²⁺ , Zn ²⁺ , Hg ²⁺ ; Particulate- Cu and Zn	Soil, waterways and estuaries
Urban solid wastes disposal	N = 0.001 – 0.2 P < 0.0001	Cu = 0,001 – 0,03 Zn = 0,001 – 0,07 Hg = 0.04	Dominant forms of N and P are too site-specific	Cu ²⁺ , Zn ²⁺ , Hg ²⁺ ; Particulate- Cu and Zn	Soil
Shrimp aquaculture	N = 1.25 – 4.09, P = 0.13 – 0.32	Cu = 38.6 – 59.8 Hg = 0.03 – 0.04 Zn = 508	PON (70%); NO ₃ ; Ammonia; NO ₂ ; POP; Phosphate	Particulate- Cu, Zn and Hg	Waterways and estuaries

Fortaleza, 1939



6,7 tPb.ano⁻¹
0,041 tHg.ano⁻¹
164 tN.ano⁻¹

Changes in soil uses

Urbanization

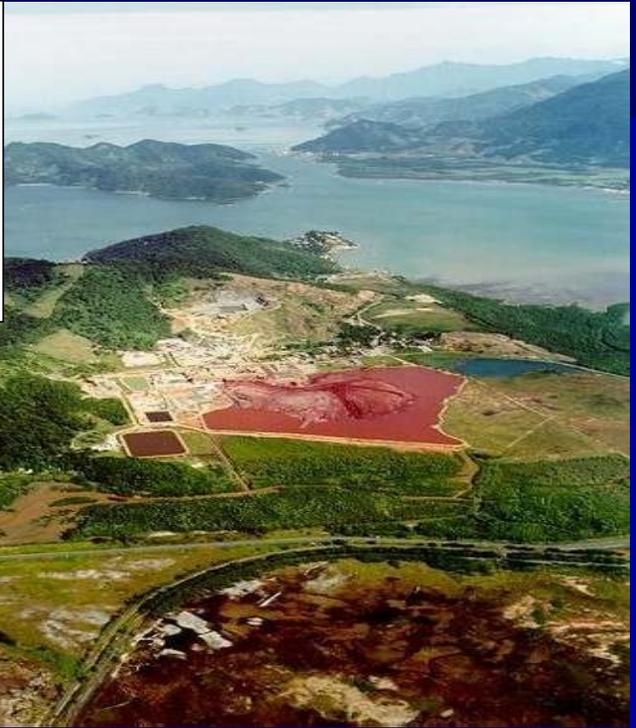
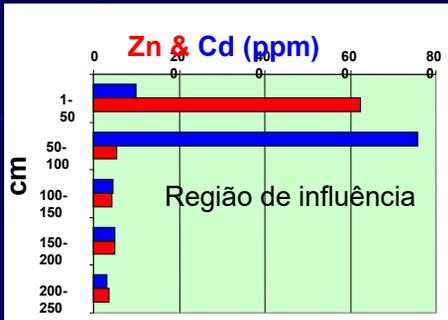
Fortaleza, 2007



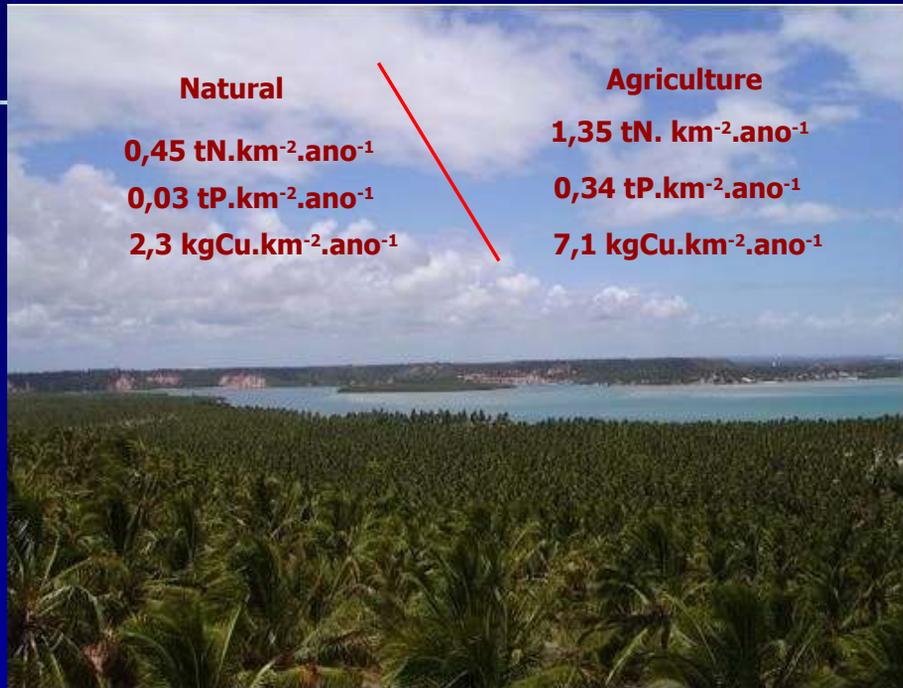
117 tPb.ano⁻¹
0,578 tHg.ano⁻¹
7.200 tN.ano⁻¹

Legacy of irresponsible technologists faces lack of governance

Industrialization

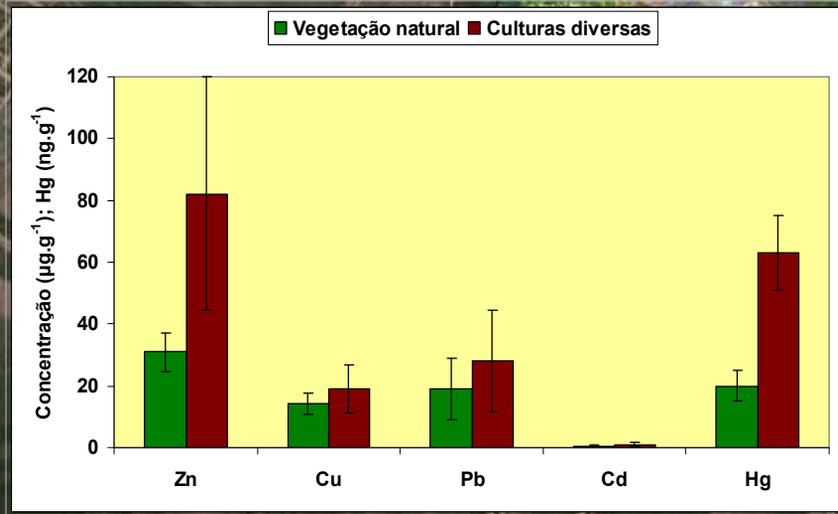


Changes in soil use: **Agriculture**



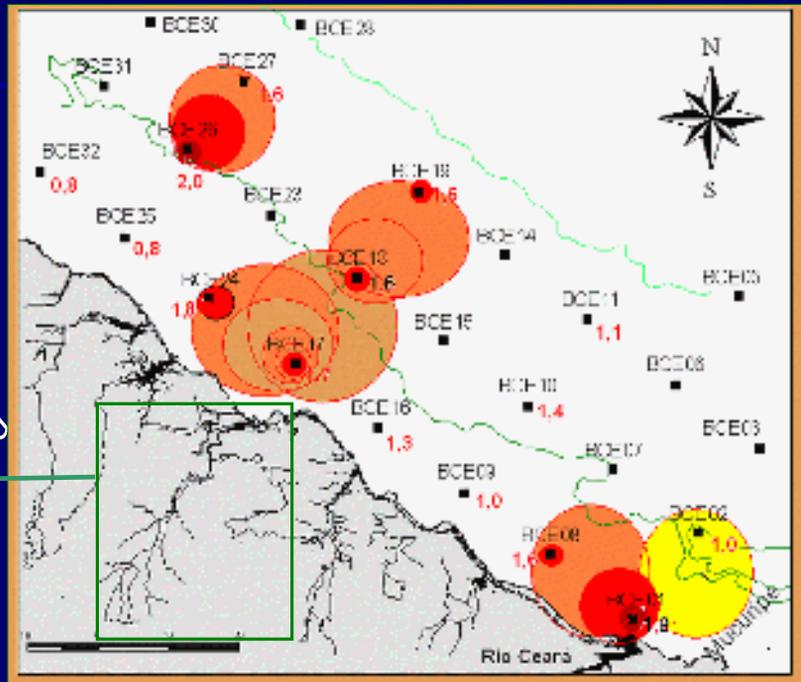
Irrigated agriculture: Vale do Acaraú (CE): metals in soils

(c.f. Lacerda & Senna, 2005, baseado em várias fontes)



The management of the area exports continental material out to shelf sediments

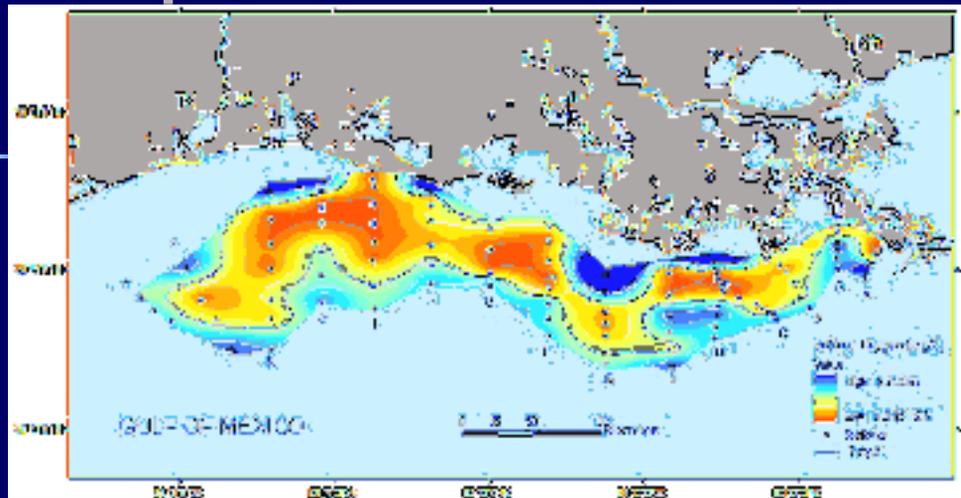
Perímetro irrigado do vale do Acaraú



A question of scale: Mississippi Delta, Gulf of Mexico, USA

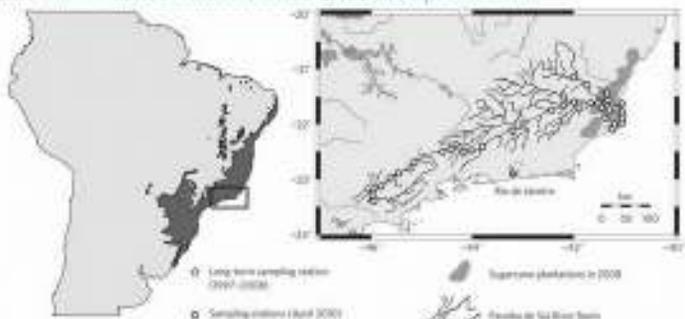


Hypoxia in coastal seas



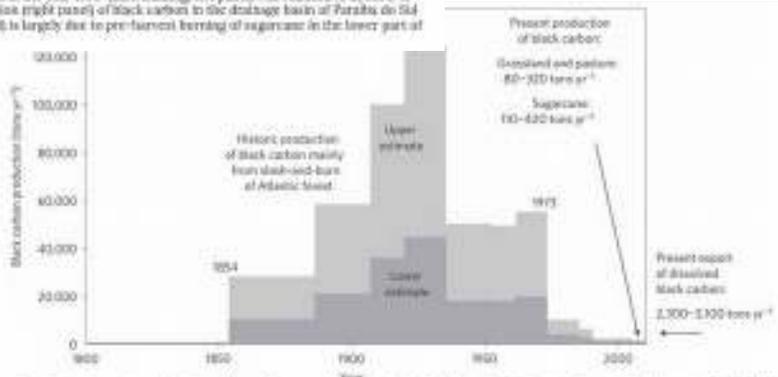
- Increasing globally due to excessive loads of nutrients and oxygen consumption
- Today, affects over 18,000 km² of the Texas-Louisiana shelf during summer

From Continuous flux of dissolved black carbon from a vanished tropical forest basin



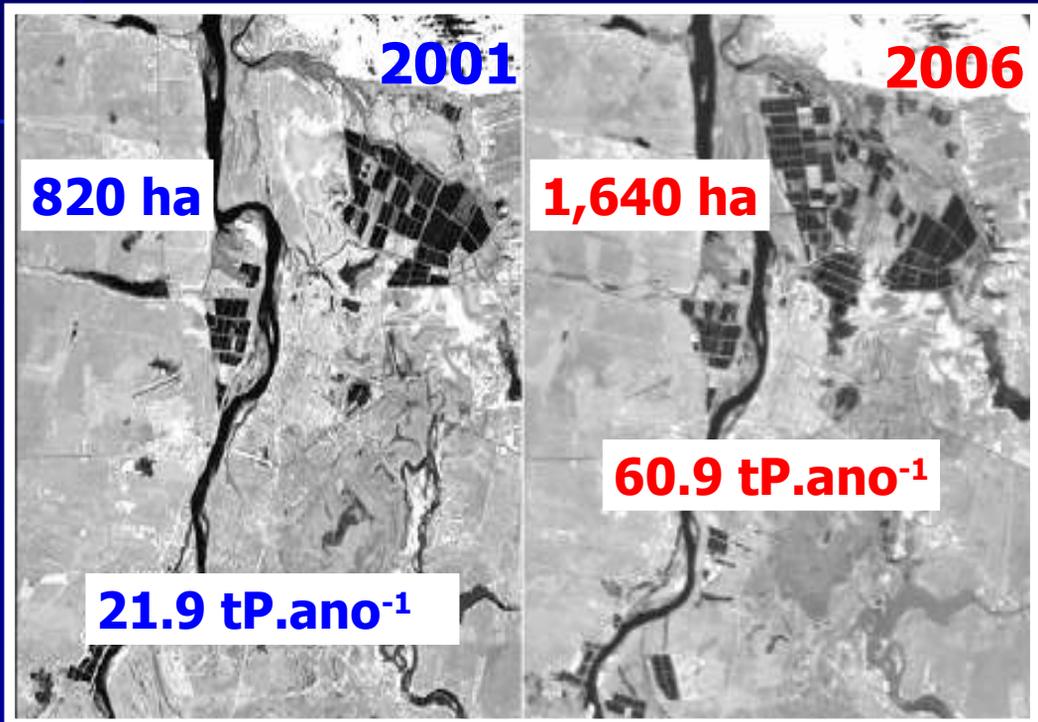
The original coverage of the tropical Atlantic forest in the year 1847 (dark shading, left panel) was reduced to about 8%, consisting of fragmented patches. Today's production (right panel) of black carbon in the drainage basin of Paraíba do Sul River (the area outlined by the box in the left panel) is largely due to pre-harvest burning of sugarcane in the lower part of the catchment area.

Continental carbon to the South Atlantic

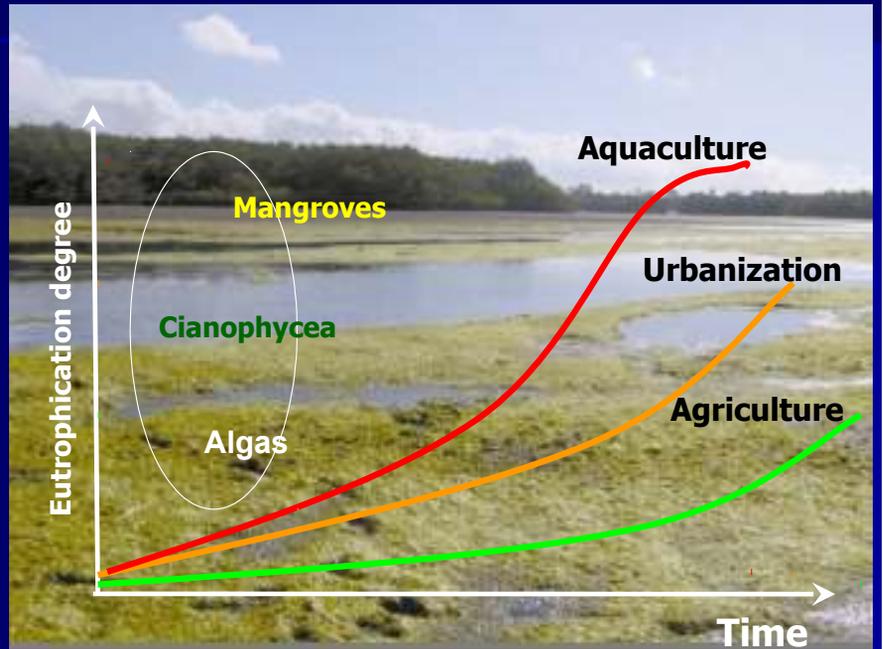


Annual production rates are for the polycyclic aromatic fraction of black carbon. The rate shown for the period 1800-1854 also represents the period 1500-1800. Black carbon was mainly produced by slash-and-burn clearing of the Atlantic forest. Today's production is mainly due to pasture management and pre-harvest burning of sugarcane.

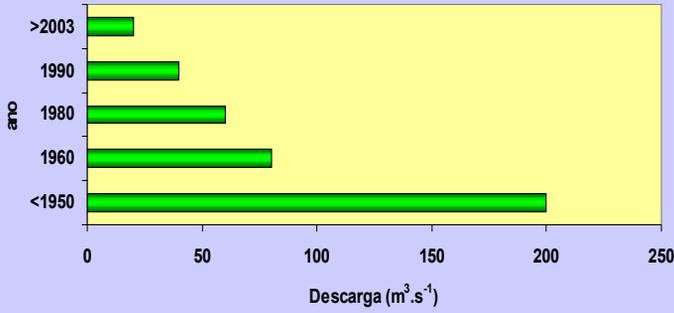
Changes in land use: **Shrimp aquaculture**
(*c.f.* Marins et al., 2009)



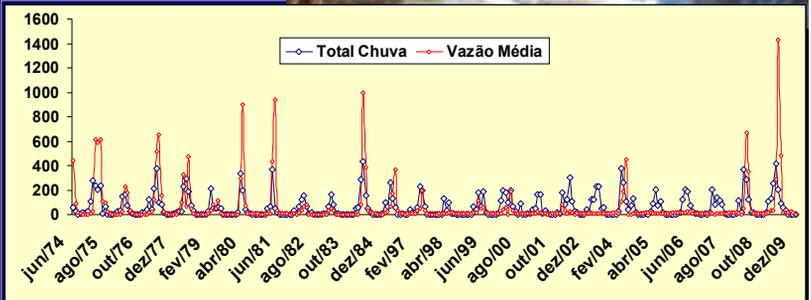
Speed of response (eutrophication) to increasing nutrient emissions from different non-industrial activities

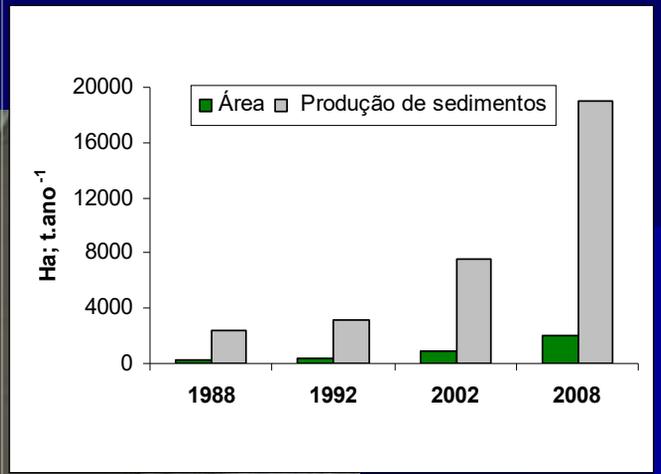
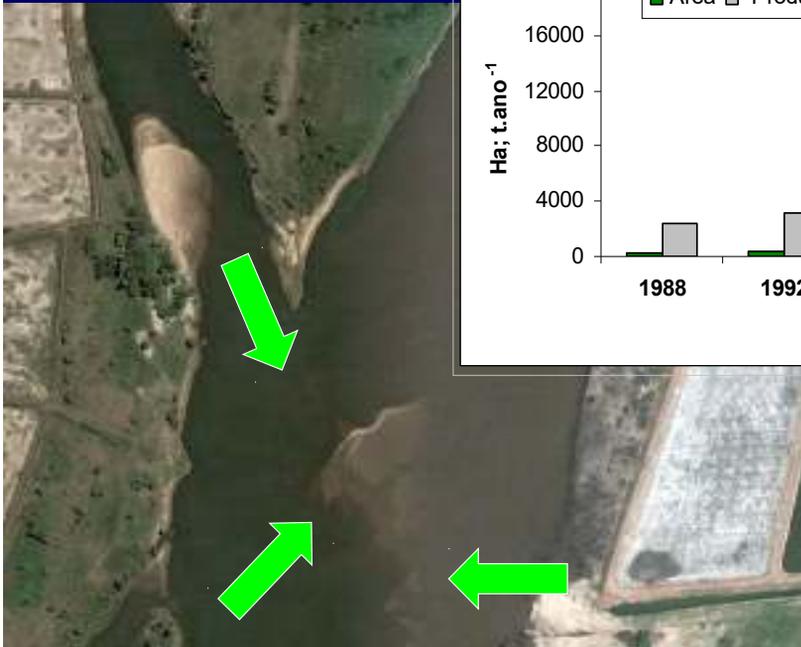


Fluxo fluvial para o Oceano Atlântico do Rio Jaguaribe, NE do Brasil durante os últimos 50 anos. (segundo Marins et al. 2002)



Dams





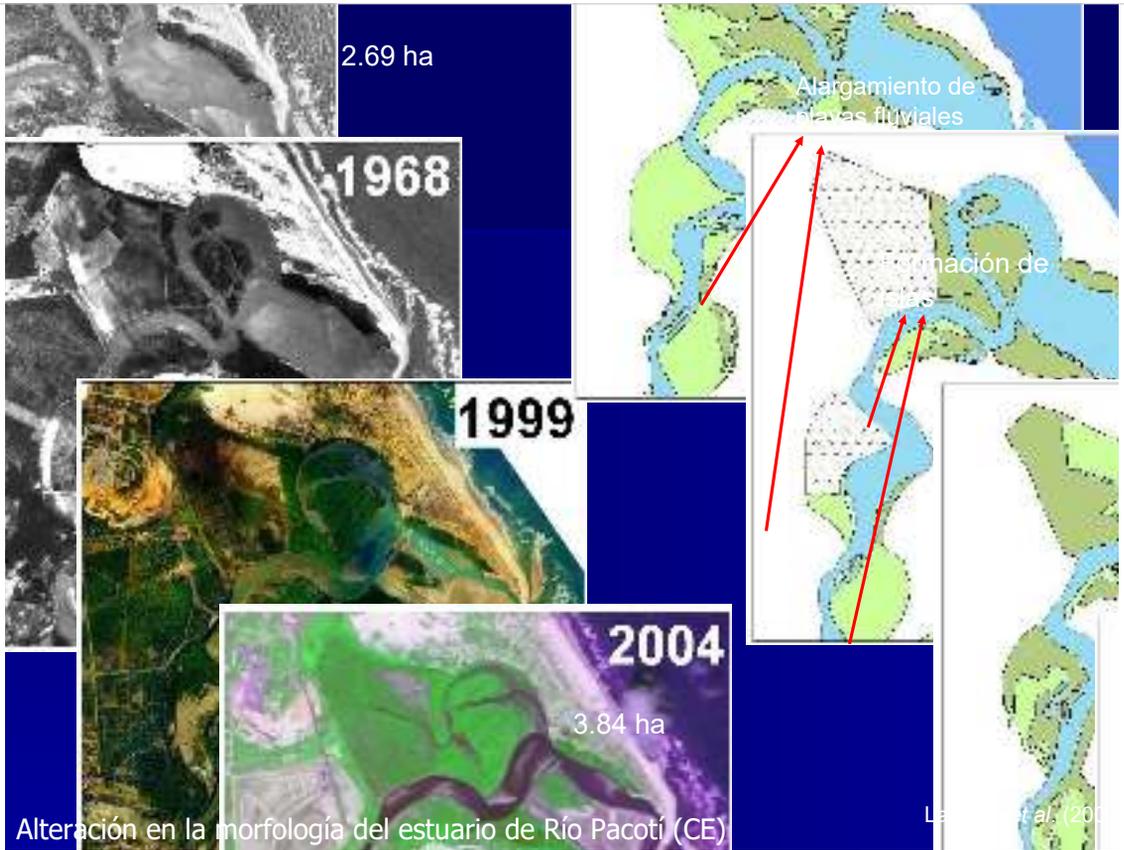
Godoy (2010)

Aquaculture & sediment production



Increasing
sedimentation areas

Godoy (2010)

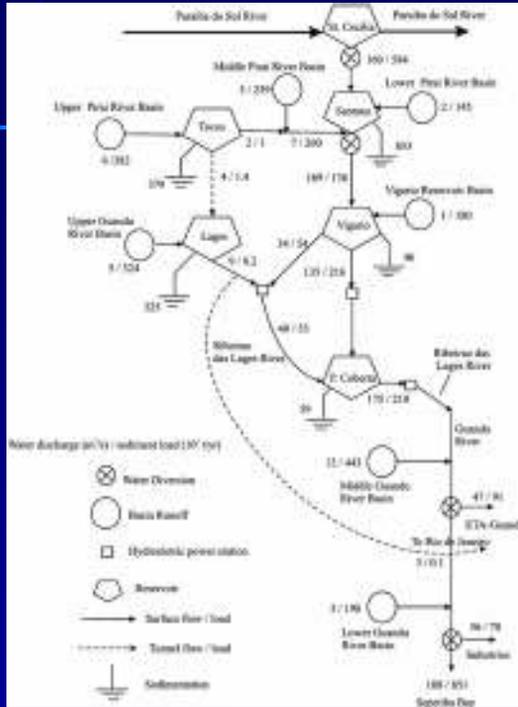




Water diversion



Contribuição de água e sedimentos pela transposição do Rio Paraíba do Sul para a Baía de Sepetiba



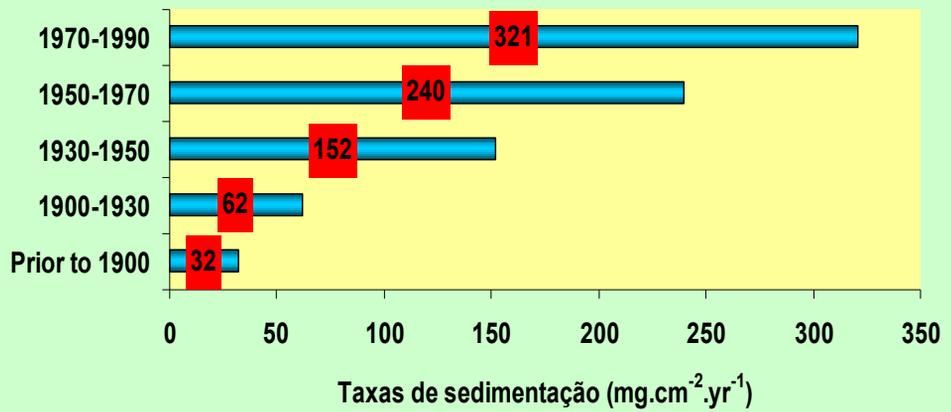
Água



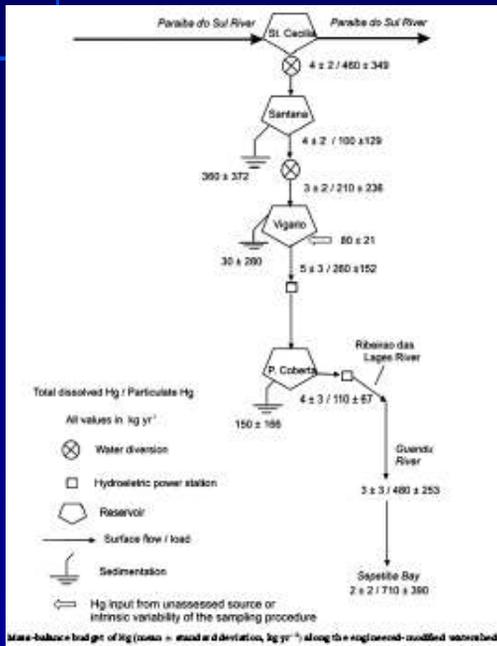
Sedimento

Molisani et al. (2007)

Mudanças nas taxas de sedimentação na Baía de Sepetiba, RJ devido a diversão de águas do Rio Paraíba do Sul (Lacerda et al. 2002)



Contribuição de Hg pela transposição do Rio Paraíba do Sul para a Baía de Sepetiba



RPS (60%)

BS (40%)

Hg-particulae

RPS (45%)

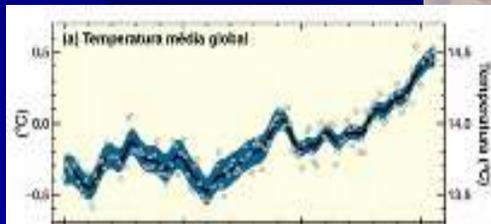
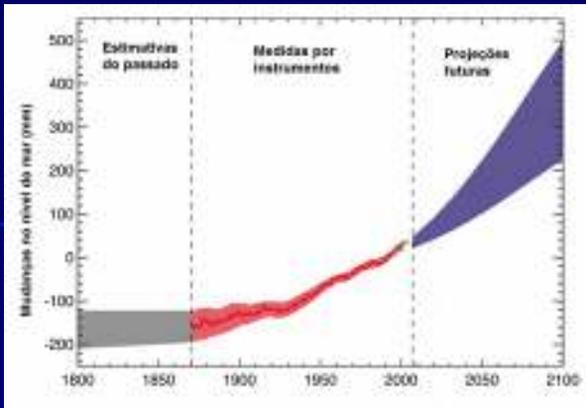
BS (55%)

Hg-dissolved

Molisani et al. (2008)

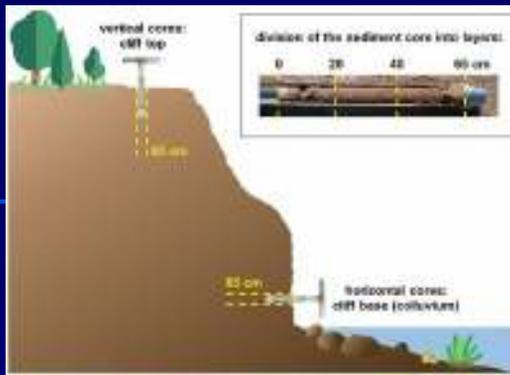
is

Global climate change: Sea level rise



Efeitos pouco óbvios: Impacto na biogeoquímica costeira

- In areas of small supply of sediments, e.g. semiarid littorals, seafront mangroves, sea cliffs; coastal deposits are increasing the remobilization of pollutants.
- On the other hand, coastal plain areas in the tropics and subtropics dominated by mangroves, sea level rise will induce mangrove migration inland, creating typical areas dominated by the mangrove metabolism (e.g. anaerobic respiration through sulfate reduction).
- Trace metal biogeochemistry and bioavailability are highly affected by the sulfate reduction metabolism.
- Part of the metal load will be accumulated as metallic sulfides in sediments, but part, with the abundant dissolved organic carbon compounds due to incomplete oxidation of organic matter, will be made more bioavailable, increasing bioaccumulation and enhancing biota and human exposure through food chains.



Sea level rise and Hg contribution through erosion
 (Kwasigroch et al., 2018 (in press))
 Up to 14.5 kg.yr⁻¹; the 3rd most important Hg source to Gdansk Bay.

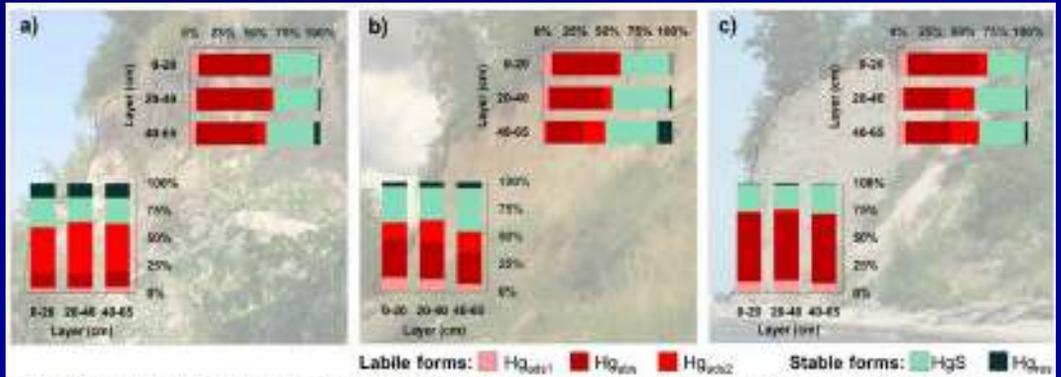
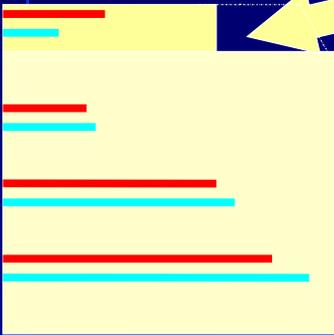


Fig. 3 The percentage of Hg fractions in horizontal and vertical profiles of investigated cliffs. a) Puck cliff, b) Osłonino cliff, c) Mecheliniki cliff

Erosion of coastal mangroves sediments in NE Brazil

Metal concentrations ($\mu\text{g/g}$)

2x 4x 6x 8x ?



— Metal A — Metal B

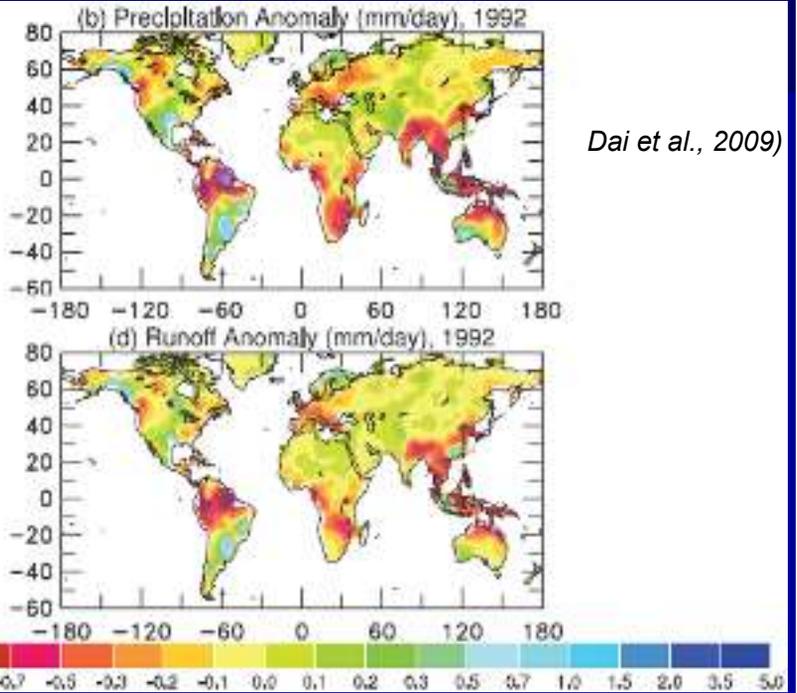
RIVER



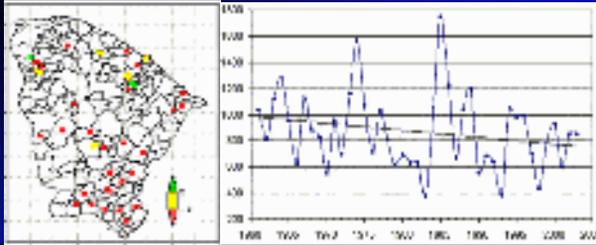
Varição do escoamento superficial e precipitação global

Out of 200 rivers, **45**, mostly in lower latitudes, have their flows decreased between 1984 and 2004, whereas **19**, have them increased

Increasing fluxes are frequently in higher latitudes and increasing flux **do not relates to increasing rainfall**, a probable reflect of ice and glacier melt.



Reduction Annual precipitation and runoff anomalies

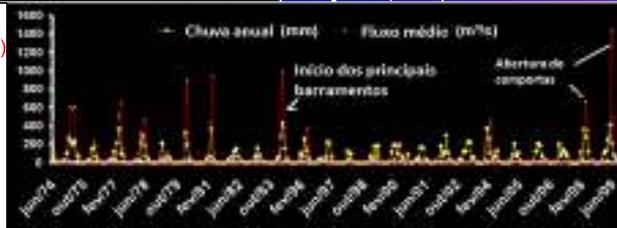
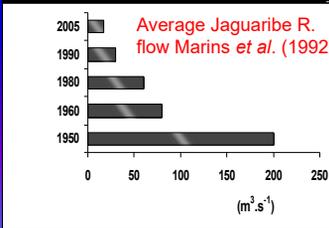


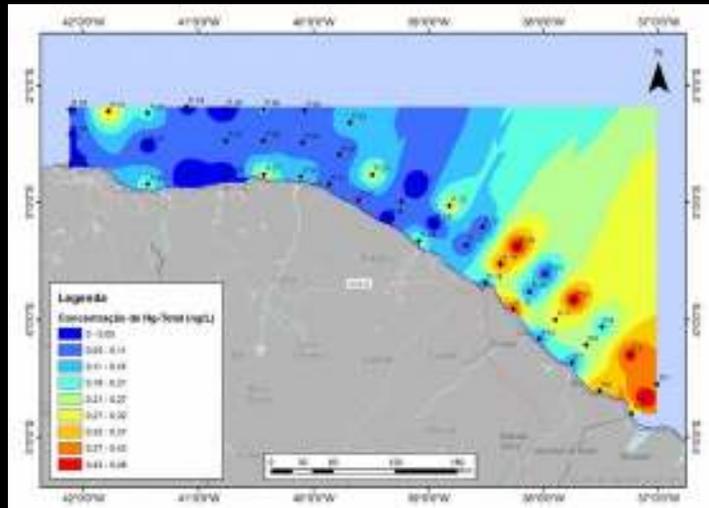
Rainfall reduction in Ceará, NE Brazil

Evolution Trend (1961 – 2008) in annual precipitation over Ceará. (4 - 5 mm.yr⁻¹ reduction) (Moncuil, 2006).

Reduction is more critical (3 times) during the dry season (Godoy *et al.*, 2010)

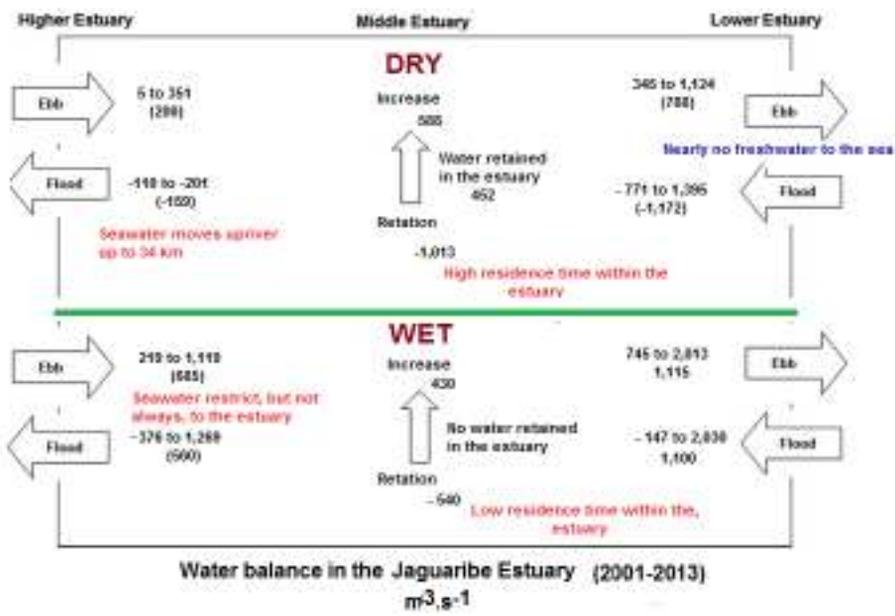
River discharges also decrease and are further affected by damming (Godoy *et al.*, 2010)



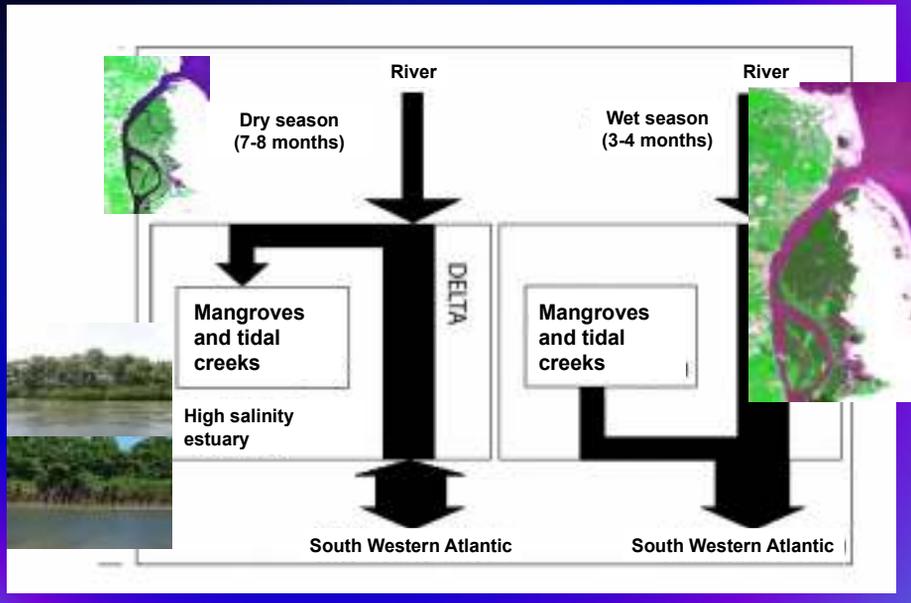


Mercury distribution in coastal waters of the semiarid northeast as a proxy of regional changes in the NE region's watersheds. The clear pattern of higher concentrations to the east are a result of such changes.

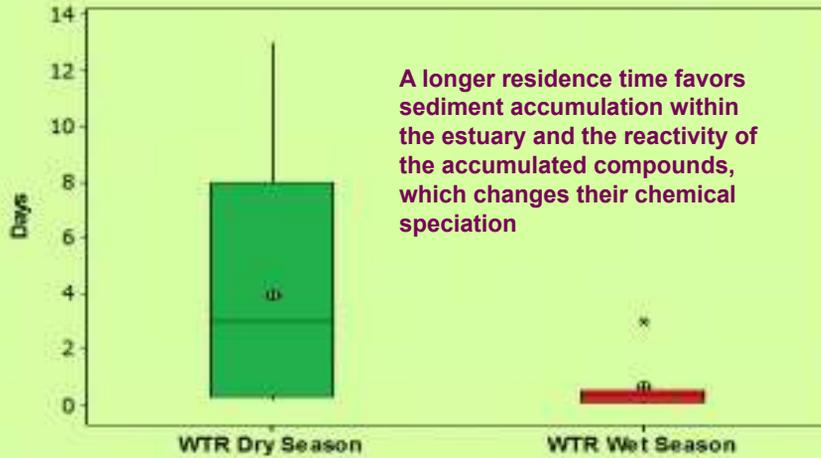
Water balance ($\text{m}^3 \cdot \text{s}^{-1}$) at the Jaguaribe estuary, NE Brazil (Dias, Lacerda & Marins 2011) pluriannual average.



Conceptual hydrodynamics model of semi-arid rivers, from Lacerda , Marins & Dias (2012)



Choking of the lower estuary due to decreasing continental runoff and increasing the strength of ocean forcing over the continental shelf, results in longer residence time of water masses within the estuary during the dry season (Lacerda, Marins & Dias, 2012)



The hydrodynamics of rivers in the semi-arid at the continent - ocean interface and therefore the distribution and biogeochemistry of their ecosystems depends on:

1 – the magnitude of the fluvial flux & continental runoff;

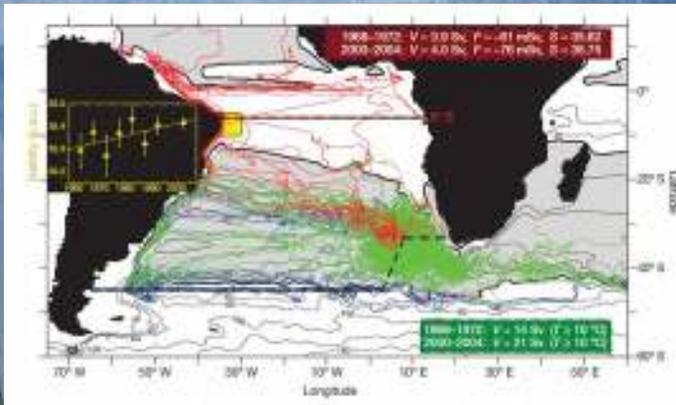
2 – the residence time of water masses in flooded areas and;

3 – sea level variation and the volume of the tidal prism.

All these variables are highly sensitive to global climate change.

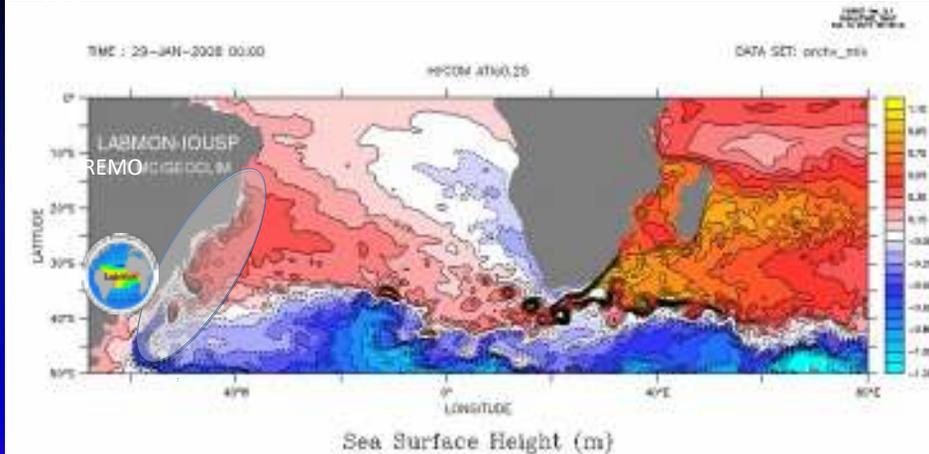
Therefore, how global climate change is already affecting the functioning of the semi-arid ecosystems and what can we expect in the future?

Apart from the effects of global and regional changes at the semi arid region itself, tele-connections & large scale transfer in the South Atlantic Ocean may also affect the residence time in estuaries and eventually the export and mobility of substances to marine food chains.



E.g. The increasing strength of the Agulhas leakage (Biaosoch, A., C.W. Böning, F.U. Schwarzcopf and J.R.E. Lutjeharms, *Nature* 462, 495-498, Nov/2009).

The impact of ocean water on continental shelf off the semi-arid coast of Brazil. Slide & Model, courtesy of Dr. Edmo Campos, USP



Surface circulation off the Brazilian coast is part of a “Super Gire” connecting the South Atlantic ocean with the Indian Ocean. The South Atlantic is the ocean where highest heat accumulation occurs due to global warming.

Indian Ocean waters “leak” to the South Atlantic, a key element in the global thermohaline circulation. Courtesy Dr. Edmo Campos, USP.

✓ Temporal and spatial distribution of continental water masses combining multi-tracers analysis and simultaneous sampling grids in river, estuary, plume and continental shelf, show freshwater plume during the rainy season and penetration of Tropical Waters (Oceanic) into the shelf. (↗ (Dias, Castro & Lacerda, 2011)



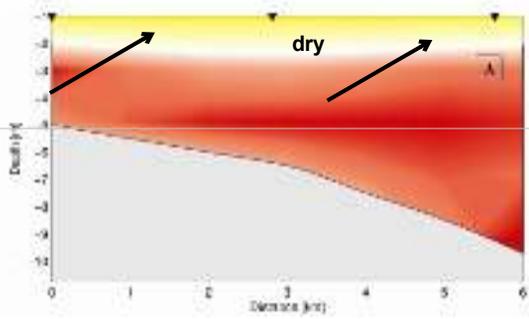
Inner shelf

dry

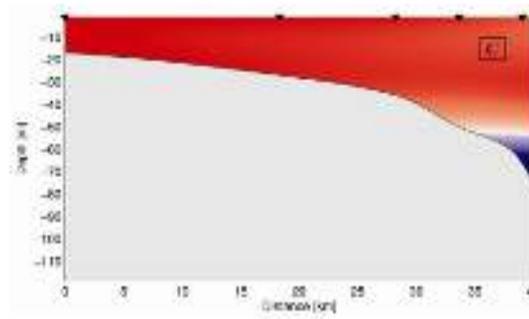
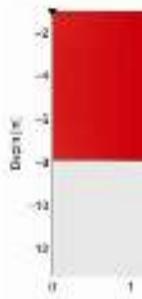
wet

Middle and outer shelf

wet



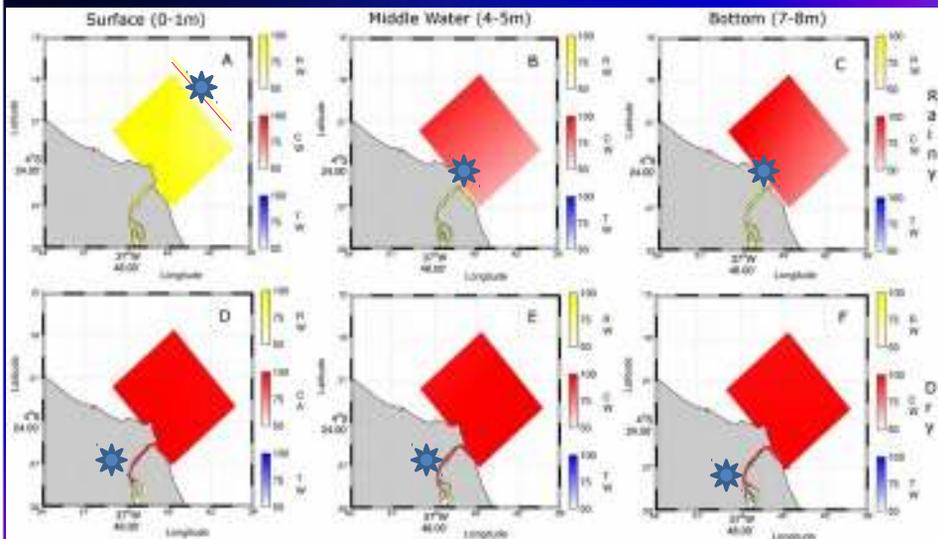
Inner Shelf



Middle and External Shelf



Choking the estuary increases water residence time, augmenting reactivity and bioavailability of substances. Stronger ocean forcing moves mixing zone and reactivity processes landward (Dias, Castro & Lacerda, 2011)

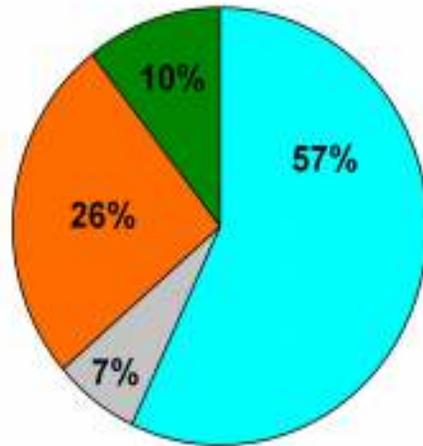
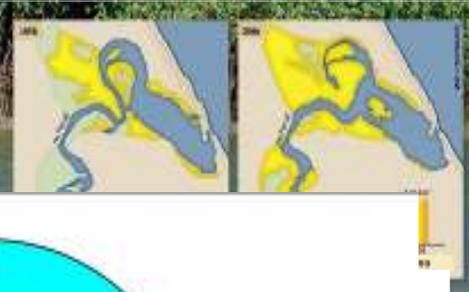


Mixing zone

What are the major impacts of the processes described above on the fate of pollutants?

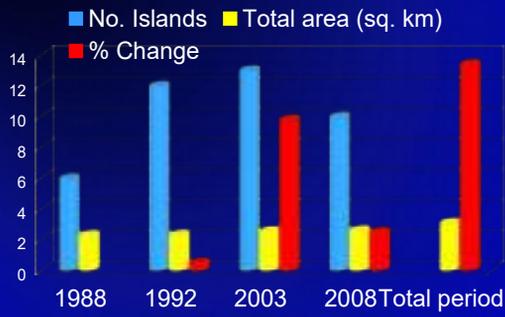
How the chemistry of pollutants responds to the increasing choking of estuaries and decreasing continental runoff, sedimentation in estuaries, mangrove expansion and longer water residence time there?

Origins of alterations identified in 41 estuaries of the semiarid littoral of NE Brazil. Comparing radar data from 1980 to Landsat, SPOT & Quickbird data from 1999 to 2013



?

Changes in island area in the Jaguaribe River estuary between 1988 and 2008 (Godoy & Lacerda, 2013)



Mangrove expansion in NE Brazil (Maia, Gentil & Lacerda, 2006)

Parameter	km	%
Total mangrove area in 1978	278	
Total mangrove area in 2004	352	
Increase (uncertainty)	74	21% (3%)



Three generations of mangroves along the Jaguaribe River, NE Brazil

Biogeochemical Scenario

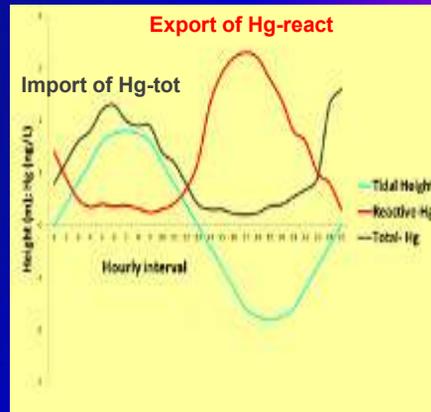
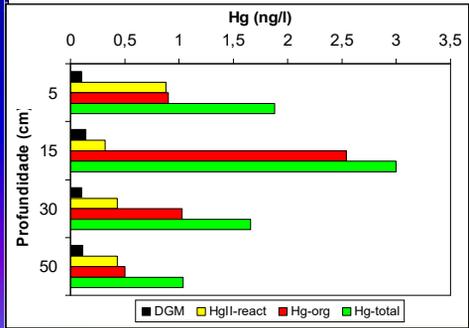
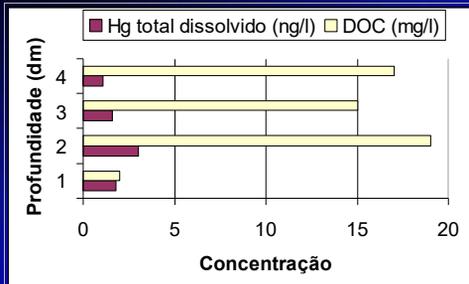
✓ Augmenting water residence time and sedimentation at the estuary increases mangrove areas and its metabolism based on dissimilatory sulfate reduction expands to larger areas.

✓ There is a larger export of DOC from the incomplete respiration of organic matter by anaerobes.

✓ Deposited metals from continental origin accumulate and suffer chemical changes instead of rapid being exported to the continental shelf.

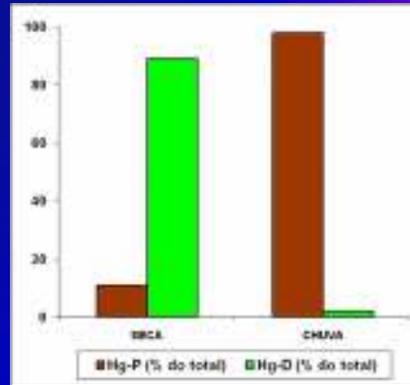
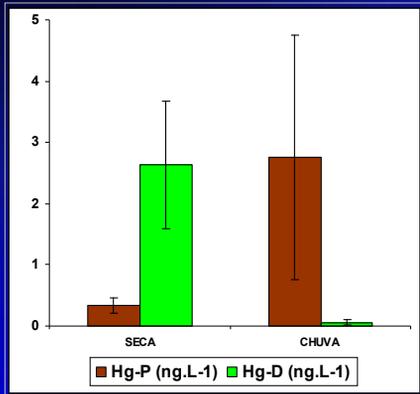


Organic-Hg complexes production in porewater facilitates Hg export from sediments



Tidal export of Hg from the from a mangrove forest (Lacerda et al., 2001)

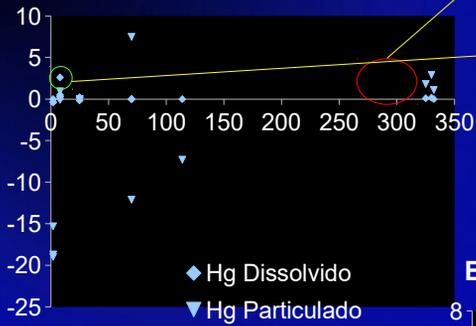
Relative Speciation of Hg in the dry and wet season at the Jaguaribe Estuary (Lacerda et al., 2013)



Dissolved Hg species dominate the flux during the dry season.

Particulate Hg species dominate the flux during the wet season.

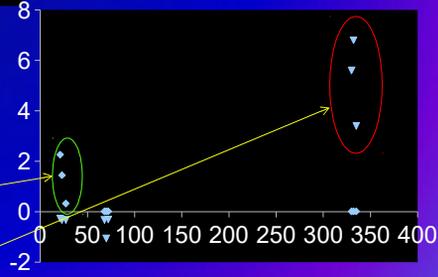
River to estuary



Export of particulate Hg from river to estuary occurs only under **intermediate and high fluvial fluxes**; Dissolved Hg export occurs with **fluvial fluxes close to zero**

Rain vs Transport

Estuary to Sea

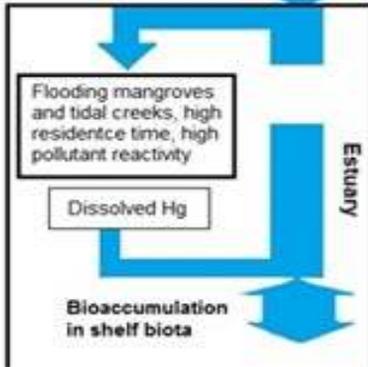


Export of dissolved Hg occurs only during the dry season with **discharge close to zero**. Particulate Hg export occurs only under **very high water discharge**

Dry season
(7-8 months)

river

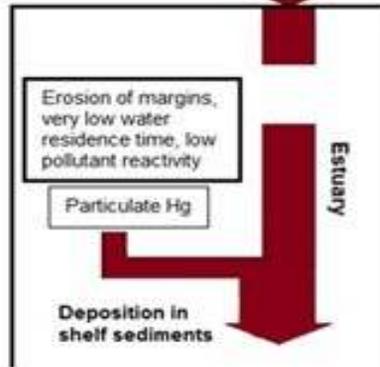
low flow



Wet season
(4-5 months)

river

high flow



Southwestern Atlantic Ocean

Mechanisms involved in the augment of Hg dissolved species (bioavailable), favored by the augment of the water residence time within the estuary

- ❖ **Desorption of Hg from suspended particles due to salinity increase and saline intrusion landward**
- ❖ **Export of pore waters enriched in DOC from ever larger mangrove forests**
- ❖ **Formation and export of soluble Hg-organic complexes**
- ❖ **Increased uptake by the phytoplankton associated with higher water transparency.**
- ❖ **Faster assimilation and accumulation in the food chain**

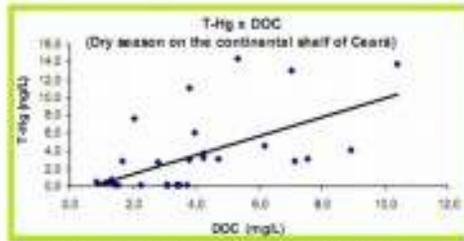
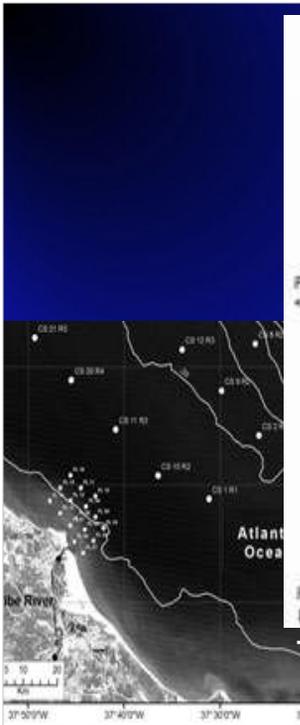


Figure 1: Correlation of T-Hg concentration (ng/L) with DOC (mg/L) ($r = 0.6003$, $n = 31$, $p < 0.05$) during the dry season on the continental shelf of Ceará - Brazil.

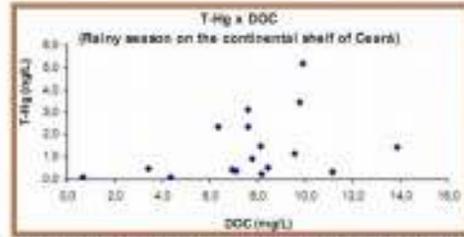


Figure 2: Correlation of T-Hg concentration (ng/L) with DOC (mg/L) ($r = 0.3604$, $n = 20$, $p < 0.05$) for the rainy season on the continental shelf of Ceará - Brazil.

**Total Hg in coastal waters off the Jaguaribe River
(Soares, Marins & Lacerda, 2011)**

Augment of water mass chocking and water residence time in estuaries.
Increasing saline intrusion and accumulation of continental materials inside the estuary

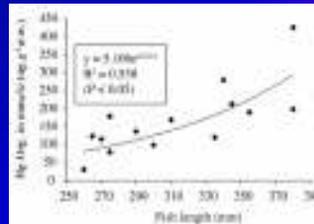


Hg-Org

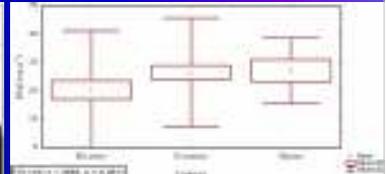
Continental fluxes may decrease in total but qualitative changes occur due to longer residence time augmenting reactive and bioavailable species (e.g. Hg)



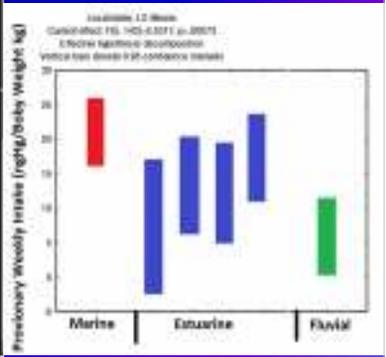
Increasing reactive species increases biological uptake, food chain transfer and human exposure.



Hg em *Cephalopholis fulva* do mar cearense (Lacerda et al., 2006)



Hg in Fish



Human exposure

Obrigado!

<http://inct.cnpq.br/web/inct-tmcocean/home/>

