Instituto de Pesquisas Energéticas e Nucleares

Applications of U and Th series nuclides in materials transfer studies performed at São Paulo State estuarine and coastal settings

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Objectives

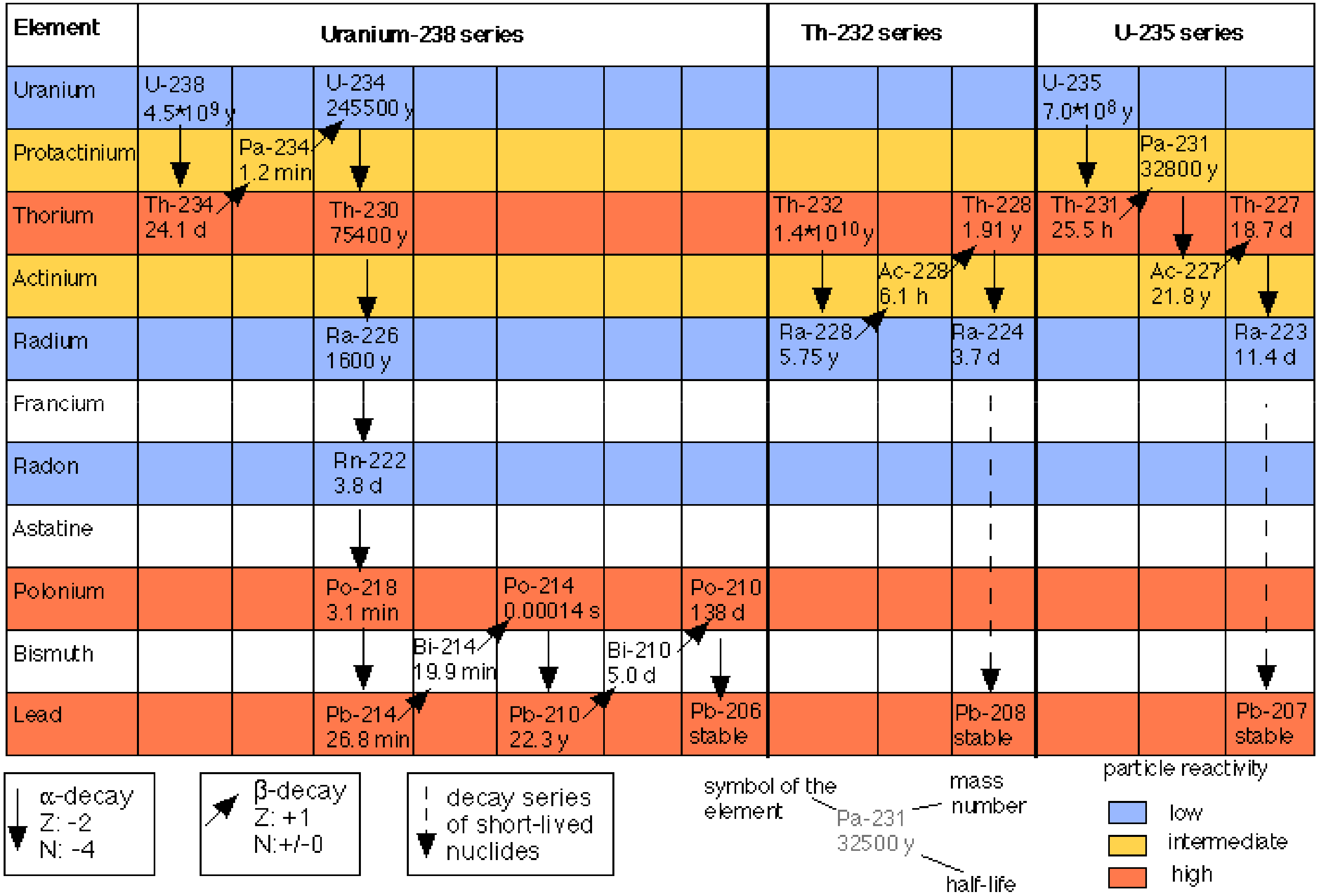
- **The main objectives of the studies performed at São Paulo State coastal and estuarine settings were to develop and improve capabilities on the application of tracer techniques to assess submarine groundwater discharge and its influence on coastal oceanographic processes.**

Introduction and significance

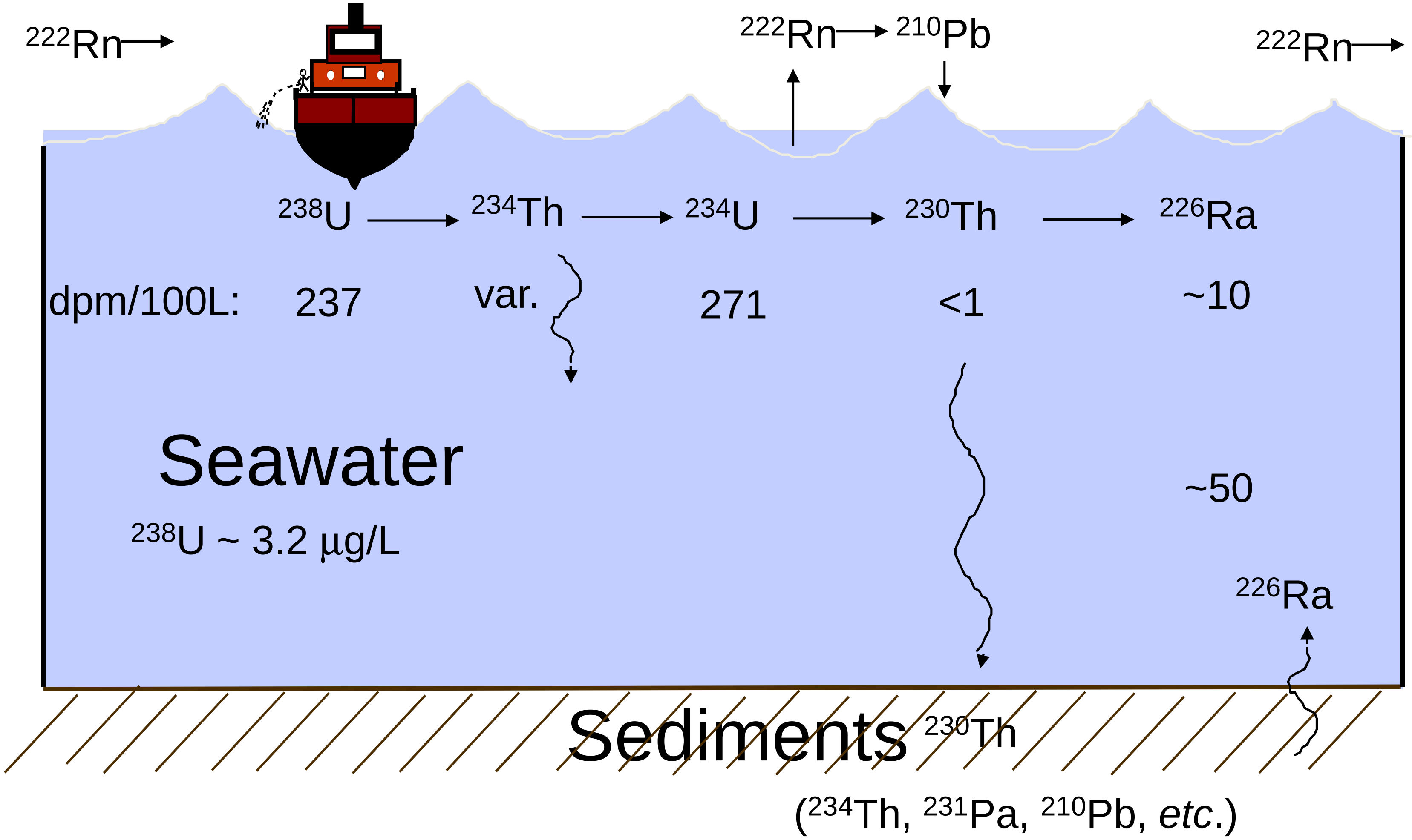
Natural radionuclides have been widely used as tracers for the investigation of open processes and coastal zone management.

Their applications both in oceanographic studies and marine contamination studies have been helping to better comprehend the processes in the water column (particle transport, carbon cycle, biogeochemical cycling, scavenging processes) or sediment dynamics processes (sinking, deposition, accumulation, transport and re-suspention).

The Natural U-Th Decay Series



U series disequilibrium in the ocean



Introduction and significance

Submarine groundwater discharge (SGD), which includes fresh water and recycled seawater, has been recognized as a widespread phenomenon that can provide important chemical elements to the coastal zones, representing an important material flux pathway from land to sea in some areas.

It may influence the geochemical cycles of some major and minor elements either by the direct discharge of fresh groundwater into the sea or by chemical reactions that occur during recirculation of seawater through a coastal aquifer system.

Introduction and significance

SGD may be a pathway for diffuse pollution to coastal marine systems, where coastal aquifers become impacted by domestic effluents (septic systems and other releases) or other sources of pollution.

Estimates of global SGD vary widely; some estimates are as high as 10% of the river flow. These fluxes also change with time due to natural, seasonal and anthropogenic variations in the source functions, such as sea level, tides, rain, permeability, porosity of the bottom sediments or dredging activities.

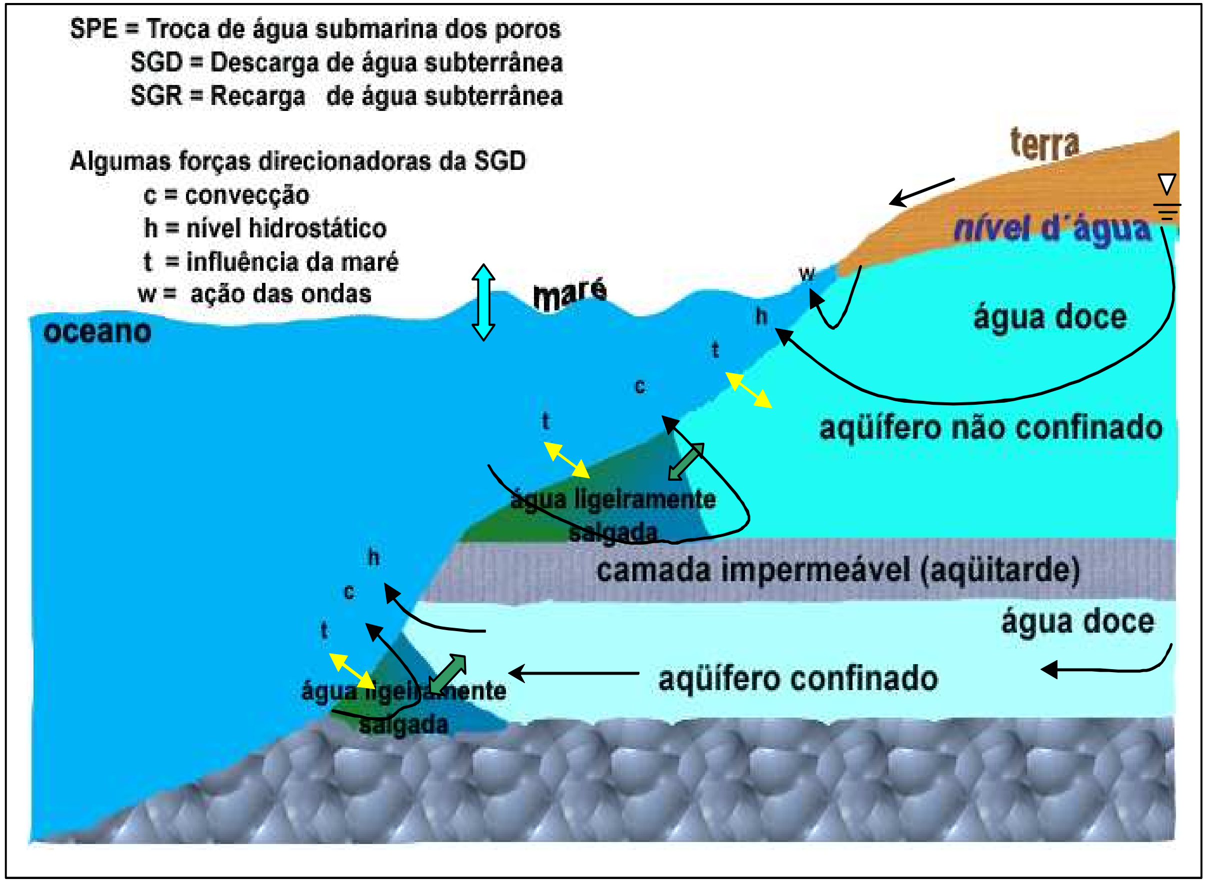
Introduction and significance

Natural radionuclides from ^{238}U and ^{232}Th decay series have been applied to trace and quantify groundwater inputs to the ocean.

Geochemical tracers, like ^{222}Rn and ^{226}Ra are advantageous for regional-scale assessments of SGD, because their signals represent values integrated through the water column that removes small-scale variations.

These radionuclides are usually enriched in groundwater compared to seawater, can be measured at very low concentrations and are conservative.

Submarine groundwater discharge (SGD)



Definition – any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force.

- SGD driven by hydraulic gradient.
- Considerable mixing with seawater.
- Oceanic forces may also drive flow, i.e., tidal pumping, wave set up.

SGD Measurement Techniques :

^{222}Rn and Ra isotopes

Advantages of ^{222}Rn

- Very high concentration in groundwater

- Low concentration in seawater

- Conservative

- Measure Rn “continuously” so can obtain good temporal resolution of processes effecting SGD

Estimating the groundwater discharge using ^{222}Rn as a natural tracer

An assessment of SGD via radon tracing involves 4 steps:

(1) measurement of the water column inventory of ^{222}Rn;

(2) an accounting of any ^{222}Rn inputs and outputs to the study area by other processes;

(3) a calculation of the total input flux of ^{222}Rn to balance the measured inventories (together with any estimated losses); and

(4) a calculation, using estimated fluid concentrations for ^{222}Rn and an advection-diffusion model, of the advective transport required to account for the estimated total input flux.

Estimating the groundwater discharge using ^{222}Rn as a natural tracer

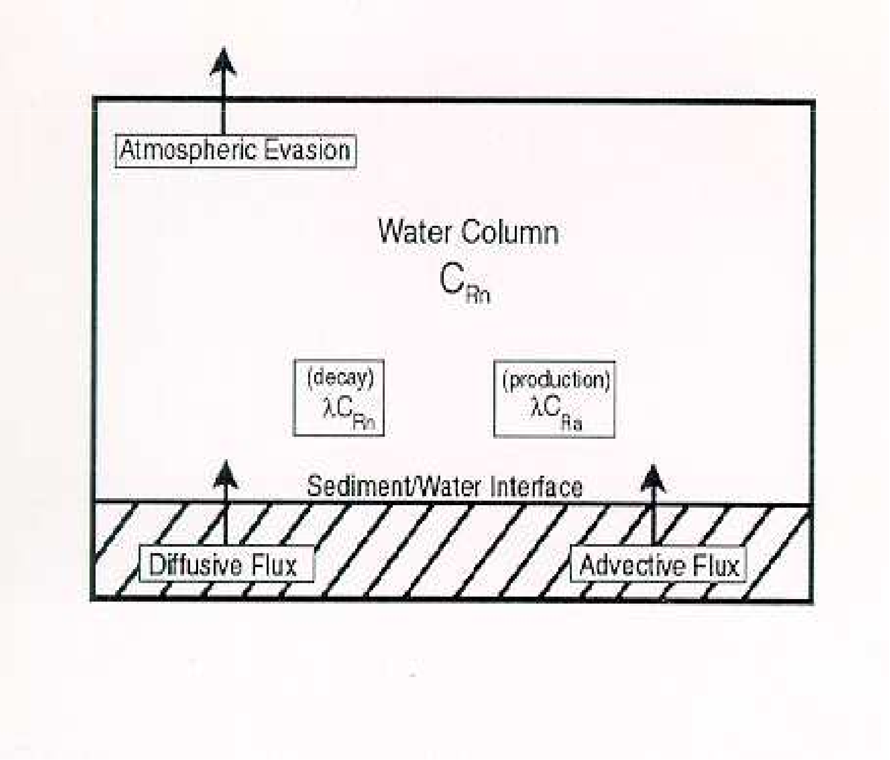
The total flux of radon required to support the inventory measured in the system can be estimated by the following equation:

$$J = \frac{I}{(1 - e^{-\lambda t} / \lambda)} \qquad (1)$$

At high values of *t* (several half-lives of ^{222}Rn), this equation reduces to I x λ.

Estimating the groundwater discharge using ^{222}Rn as a natural tracer

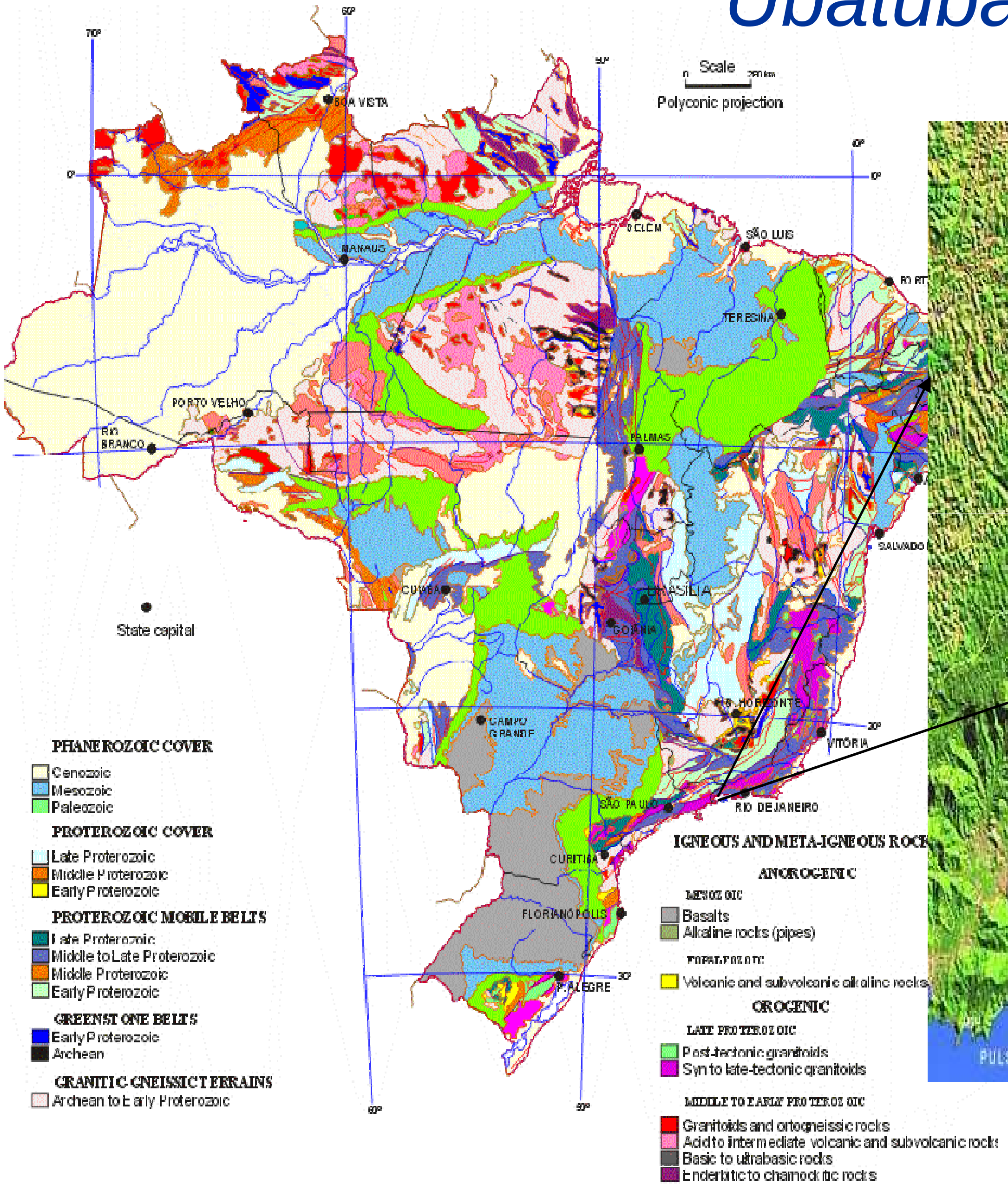
With this estimate of the required total benthic flux of radon, calculations can be made of the advective component required by using an advection-diffusion equation:



$$\frac{dC}{dt} = K_z \frac{\partial^2 C}{\partial z^2} + \omega \frac{\partial C}{\partial z} + P + \lambda C \qquad (2)$$

$$C = \frac{(Co - Ceq)\,(e^{\frac{z}{2z*}})\,\sinh(\frac{A(zeq - z)}{2z*})}{\sinh(\frac{Azeq}{2z*})} \qquad (3)$$

Assessment of the Rn-222 distributions Ubatuba, São Paulo

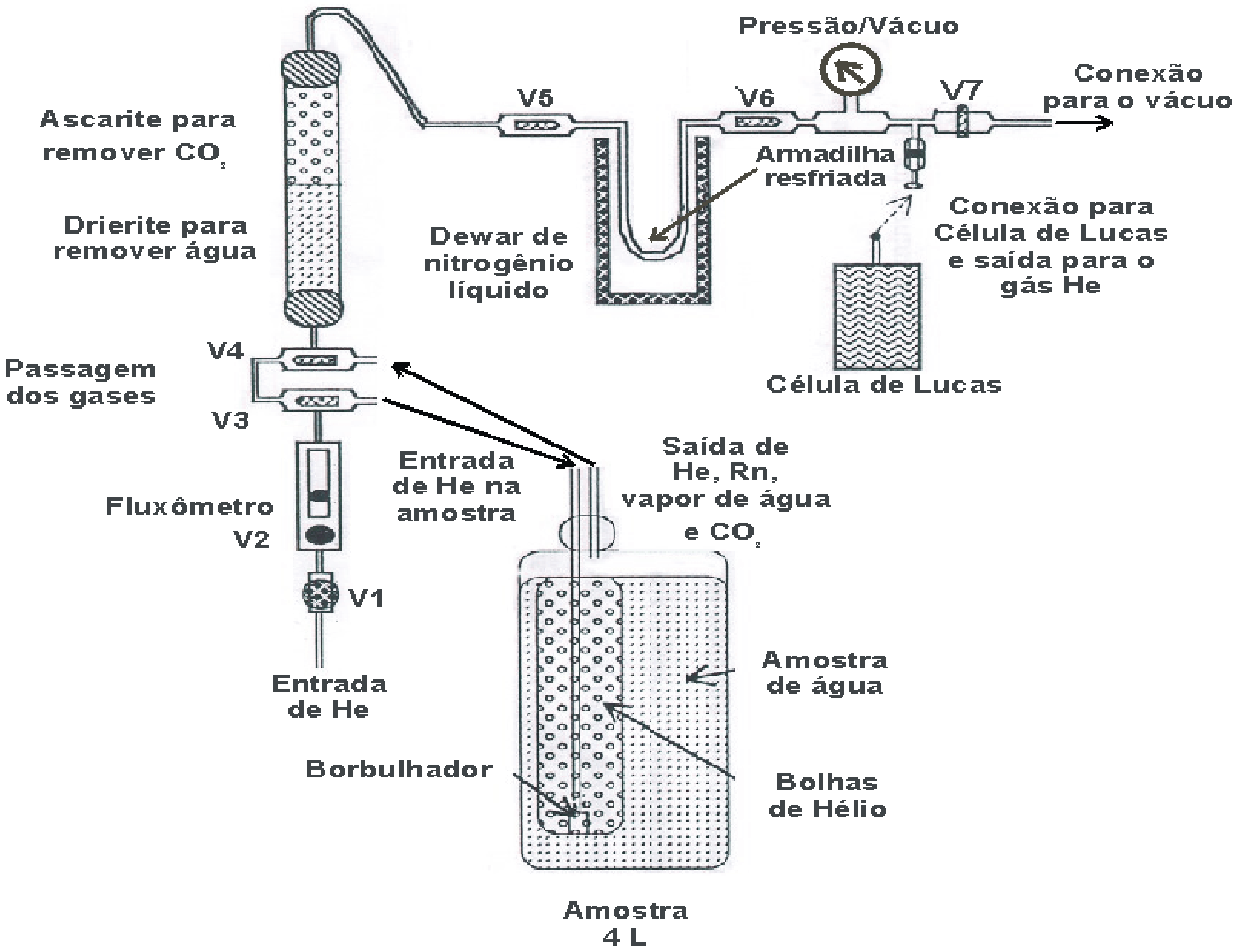


^{222}Rn as a tracer of SGD – scenario Ubatuba



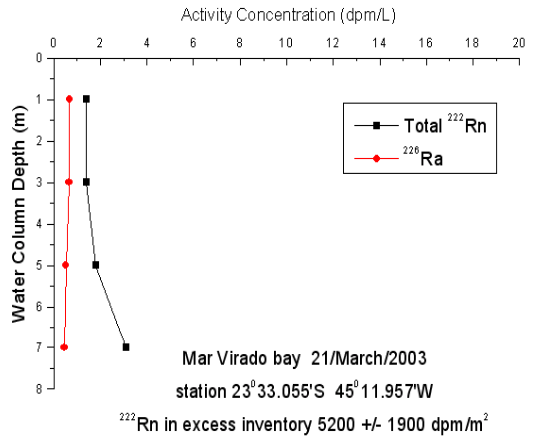


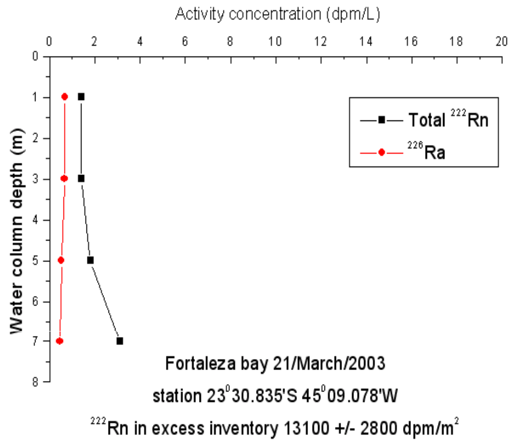

Extraction of ^{222}Rn from seawater/groundwater samples by emanometry

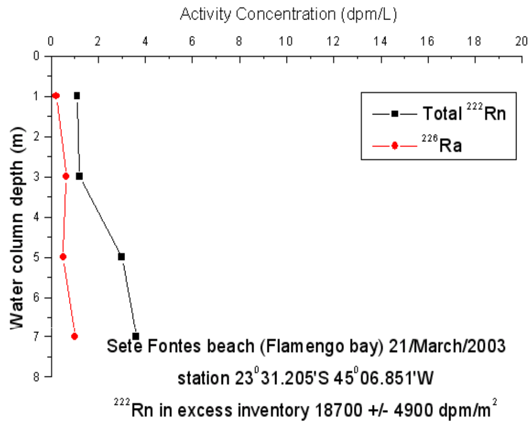


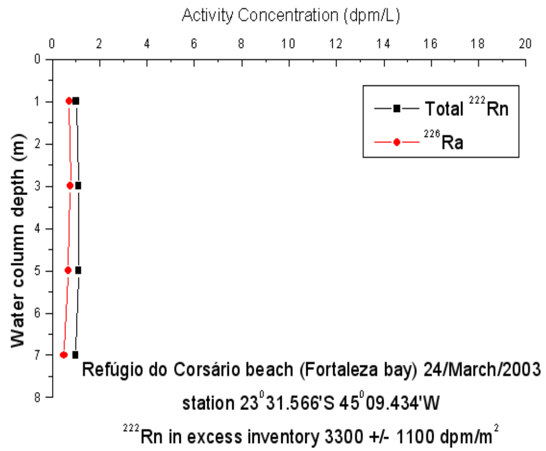
Sediment sample	C_{eq} (dpm m^{-3})	Porosity	C_o (dpm m^{-3})	
Flamengo Bay	$1,8 \times 10^5$	0,51	$1,9 \times 10^4$	
Fortaleza Bay	$8,5 \times 10^4$	0,49	$7,8 \times 10^3$	
Mar Virado Bay	$1,3 \times 10^5$	0,57	$3,0 \times 10^3$	
Ubatuba Bay	$1,5 \times 10^5$	0,62	$8,5 \times 10^3$	
Ubatuba IOUSP Marine Lab	$9,9 \times 10^4$	0,41	$8,5 \times 10^3$	

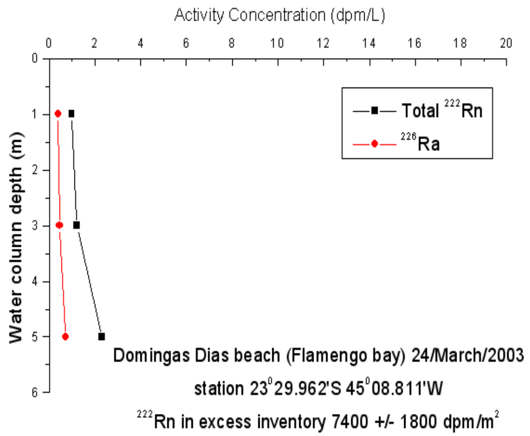
^{222}Rn vertical profiles

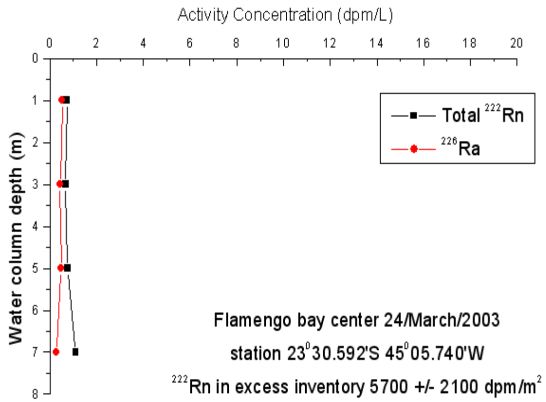




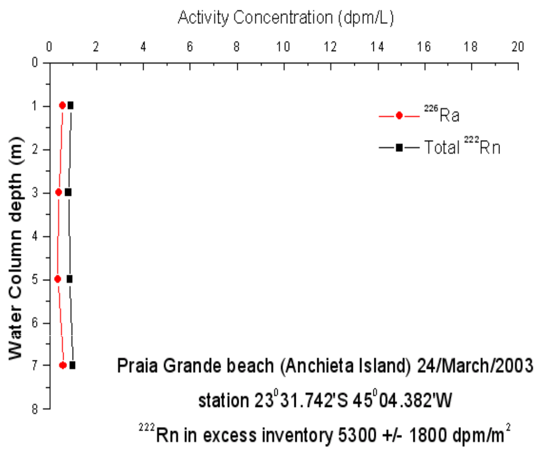


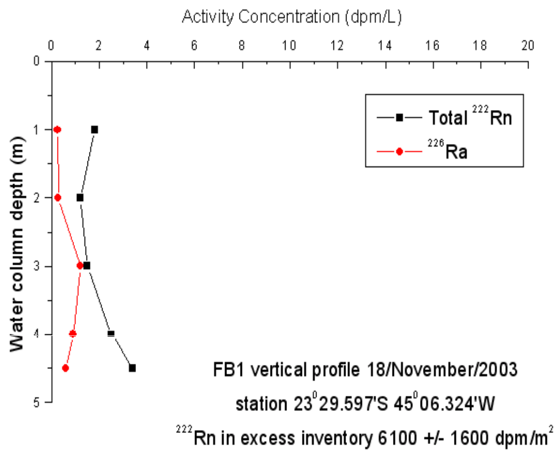


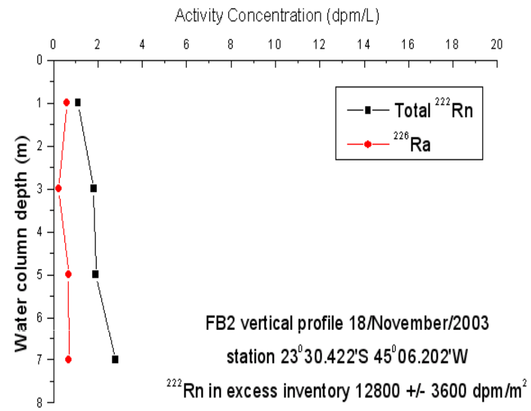


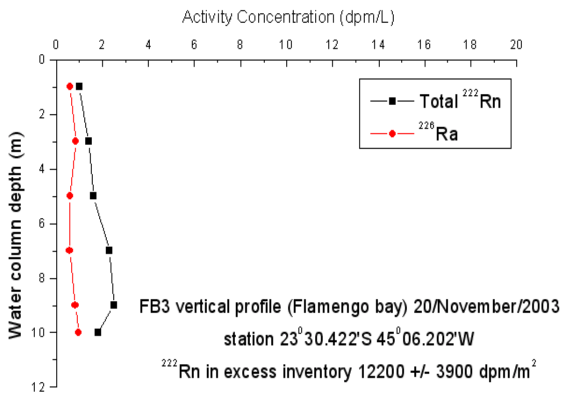


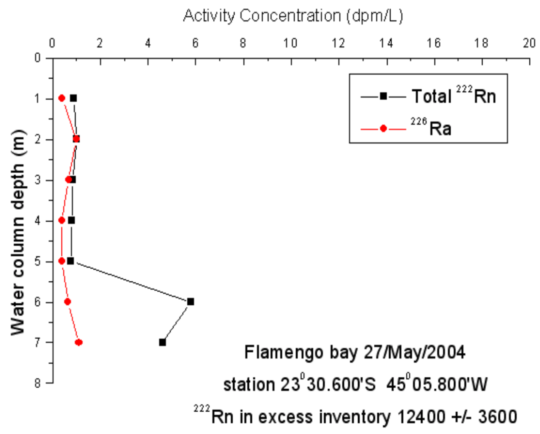
^{222}Rn vertical profiles











VERTICAL PROFILE Depth (m)	$I^{222}Rn$ excess (dpm m^{-2})	Flux ^{222}Rn excess (dpm m^{-2} d^{-1})	SGD (ω) (cm d^{-1})
March 2003			
Mar Virado Bay (8 m)	5.200 ± 1.900	941 ± 344	0,36
Fortaleza Bay (8 m)	13.100 ± 2.800	2.371 ± 507	1,3
Sete Fontes Beach (Flamengo Bay) (8 m)	18.700 ± 4.900	3.385 ± 887	1,9
Refúgio do Corsário Beach (Fortaleza Bay) (8 m)	3.300 ± 1.100	597 ± 199	0,06
Domingas Dias Beach (Flamengo Bay) (6 m)	7.400 ± 1.800	1.339 ± 326	0,65
Flamengo Bay center (8 m)	5.700 ± 2.100	1.032 ± 380	0,43
Grande Beach (Anchieta Island) (8 m)	5.300 ± 1.800	952 ± 326	0,37
November 2003 **Flamengo Bay**			
FB1 (5 m)	6.100 ± 1.600	1.104 ± 290	0,48
FB2 (8 m)	12.800 ± 3.600	2.317 ± 652	1,3
FB3 (11 m)	12.200 ± 3.900	2.208 ± 706	1,2
May 2004 **Flamengo Bay**			
FL (9 m)	12.400 ± 3.600	2.244 ± 652	1,2

Ra isotope disequilibrium to delineate SGD

and coastal water mixing rates

The knowledge of the four natural Ra isotopes in aqueous systems can be used to constrain important environmental processes occurring at the land-sea margin.

U and Th Decay Series

$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta} {}^{234}U \xrightarrow{\alpha} {}^{230}Th \xrightarrow{\alpha} {}^{226}Ra \xrightarrow{\alpha} {}^{206}Pb$

>4.5 billion years

$^{235}U \xrightarrow{\alpha} {}^{231}Th \xrightarrow{\beta} {}^{227}Th \xrightarrow{\alpha} {}^{223}Ra \xrightarrow{\alpha} {}^{207}Pb$

>700 million years

$^{232}Th \xrightarrow{\alpha} {}^{228}Ra \xrightarrow{\beta} {}^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{208}Pb$

>14 billion years

Radium Isotopes

Radium Isotope	Half life	Emission	Decay Series
^{223}Ra	11.34 d	Alpha	^{227}Th
^{224}Ra	3.64 d	Alpha	^{228}Th
^{226}Ra	1622 y	Alpha	^{230}Th
^{228}Ra	5.77 y	Beta	^{232}Th

Ra isotopes

Two main geochemical characteristics control the production and input of Ra isotopes in coastal areas:

- the existence of particle-reactive Th isotopes in sediments as its direct radiogenic parents;

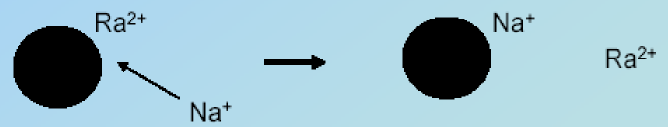
- vastly different environmental behaviour of Ra in fresh water and salt water media.

Redox State and Speciation

- Ra is not redox reactive and it is only found in an oxidation state of 2+
- Co-precipitates with $CaCO_3$ and with $BaSO_4$
- Forms soluble compounds with NO_3^-, Cl^-, IO_4^-
- Possible adsorption to ferric oxide and organic matter

Interactions with Surfaces

- Ra input into the ocean is from decay of Th in sediment.
- Ra adsorbs to sediment in rivers and desorbs in water with increasing ionic strength.
- Particle size effects – smaller particle more Ra desorbs (binding sites to size ratio)



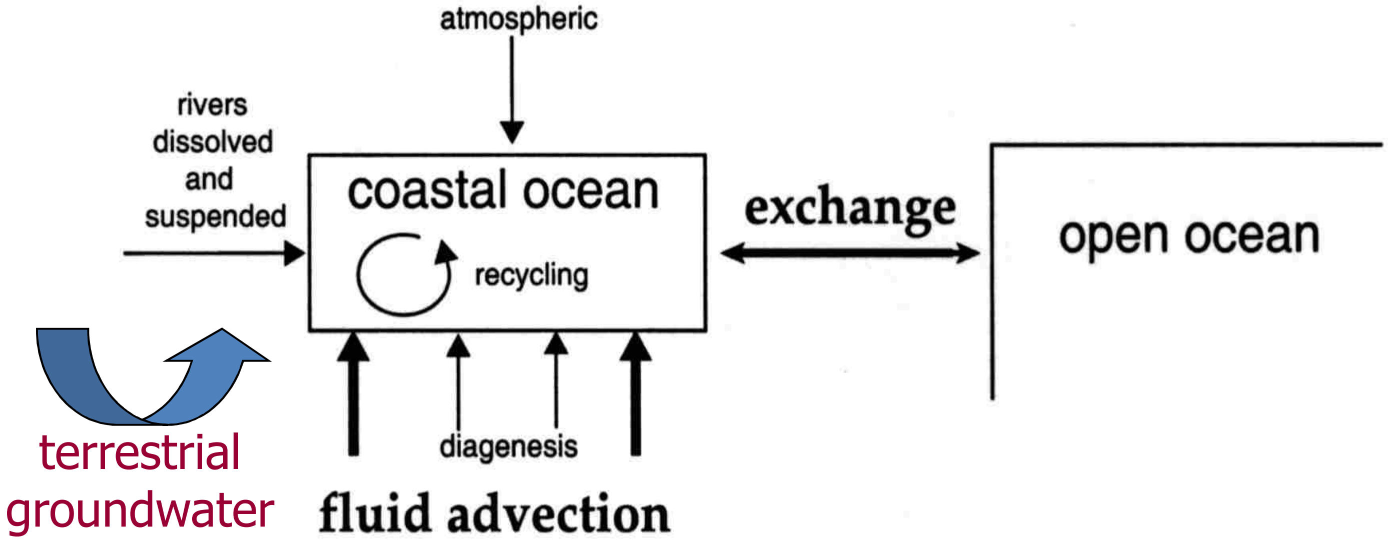
Ra isotope disequilibrium to delineate SGD and coastal water mixing rates

Shore-perpendicular profiles of ^{223}Ra and ^{224}Ra in surface waters along the coast may be modeled to yield eddy diffusion coefficients.

Coupling the exchange rate with offshore concentration gradients, the offshore fluxes of dissolved materials are estimated.

Ra isotope disequilibrium to delineate SGD and coastal water mixing rates

High Ra ←----------------→ Low Ra



Source of high Rn and Ra

^{223}Ra $T_{1/2}$ = 11 d

^{224}Ra $T_{1/2}$ = 3.6 d

Short-lived Ra isotopes on right time scale for coastal mixing

Ra isotope disequilibrium to delineate SGD and coastal water mixing rates

The Ra distribution may be expressed by a simple one-dimensional horizontal diffusion model, in which the distribution is in balance between eddy diffusion and radioactive decay:

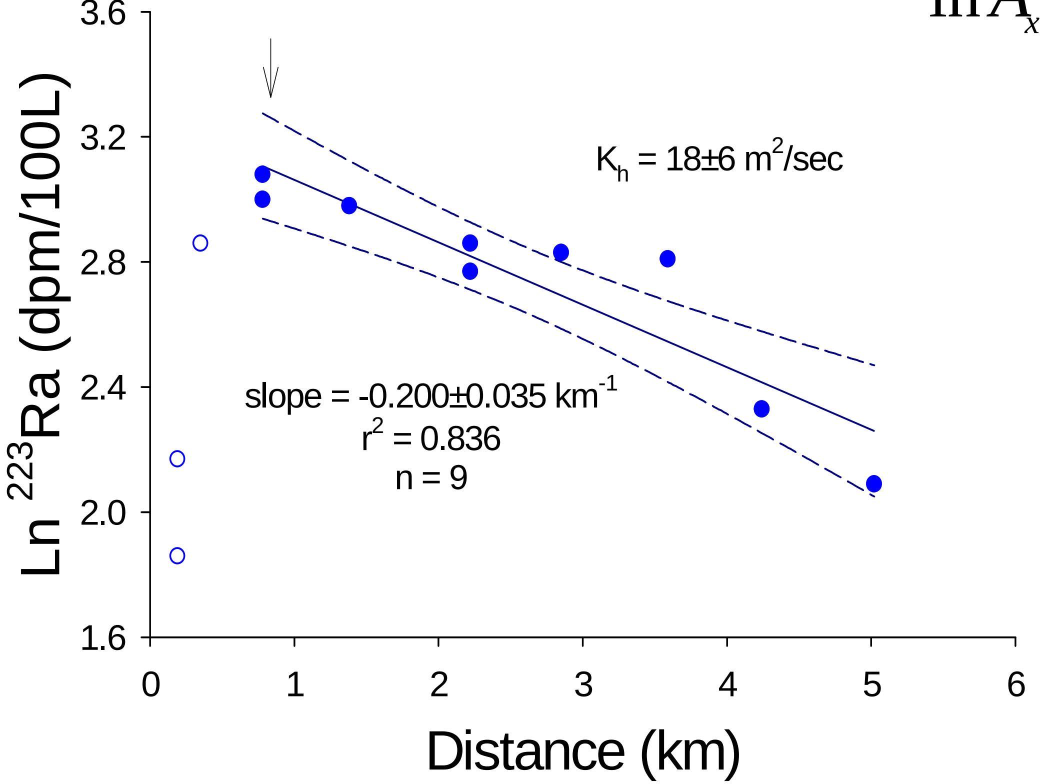
$$\frac{dA}{dt} = K_h \frac{\partial A}{\partial x^2} - \lambda A \qquad (1)$$

.

$$A_x = A_0 \exp\left[- x\sqrt{\frac{\lambda}{K_h}} \right] \qquad (2)$$

$$\left[\frac{^{224}Ra}{^{223}Ra}\right]_{obs} = \left[\frac{^{224}Ra}{^{223}Ra}\right]_i \cdot \frac{e^{-\lambda_{224} t}}{e^{-\lambda_{223} t}} \qquad (3)$$

^{223}Ra distribution offshore



$$\ln A_x = \ln A_0 - x\sqrt{\frac{\lambda}{K_h}}$$

$$m = \sqrt{\frac{\lambda}{K_h}}$$

Mixing coefficient x ^{226}Ra gradient = offshore flux -- must be balanced by coastal inputs as SGD.

Divide by groundwater conc. for estimate of water flux.

Using Ra isotopes to study coastal dynamics

Scenario – Ubatuba

Methodology to determine Ra isotopes

- large volume seawater samples (60-200 L) from 1-5 m below the surface into plastic drums.

- record the sample volume and percolate seawater through a column of manganese coated acrylic fibre to quantitatively remove radium from seawater.

- temperature and salinity profiles at each station using a CTD. Collect also samples for salinity and nutrients in each station.

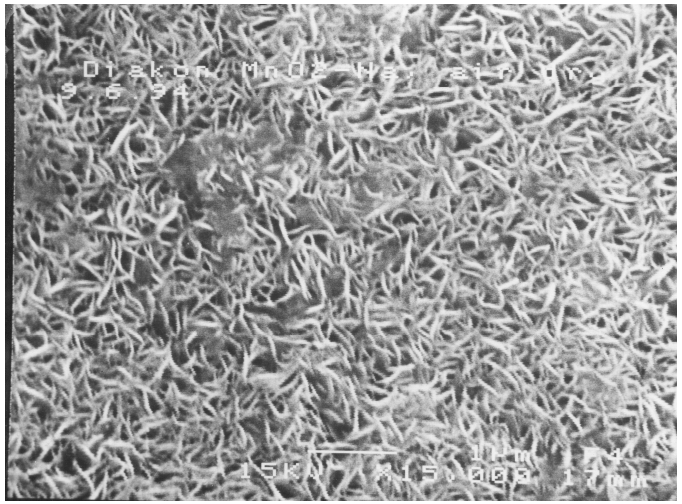
- additional samples from a set of monitoring wells and from seepage meters.

Methodology to determine Ra isotopes

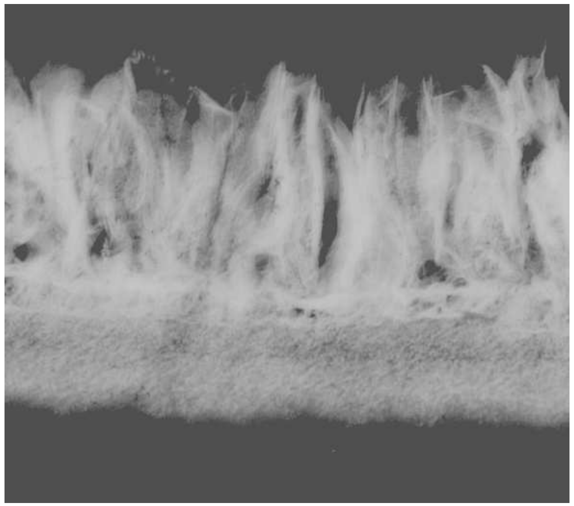
In an onshore laboratory each Mn fiber sample is partially dried with a stream of air and placed in an air circulation system.

He is circulated over the Mn fiber to sweep ^{219}Rn and ^{220}Rn generated by ^{224}Ra and ^{223}Ra decay in a 1.1 L scintillation cell. The alpha particles from the decay of radon and its daughters are recorded by a photomultiplier tube (PMT) attached to the scintillation cell.

Signals from the PMT are routed to a delayed coincident counter system adapted for Ra measurements.



Top view (width 7.7 mm)



Side view (w=0.8 mm)

90% Extraction Efficiency for Ra

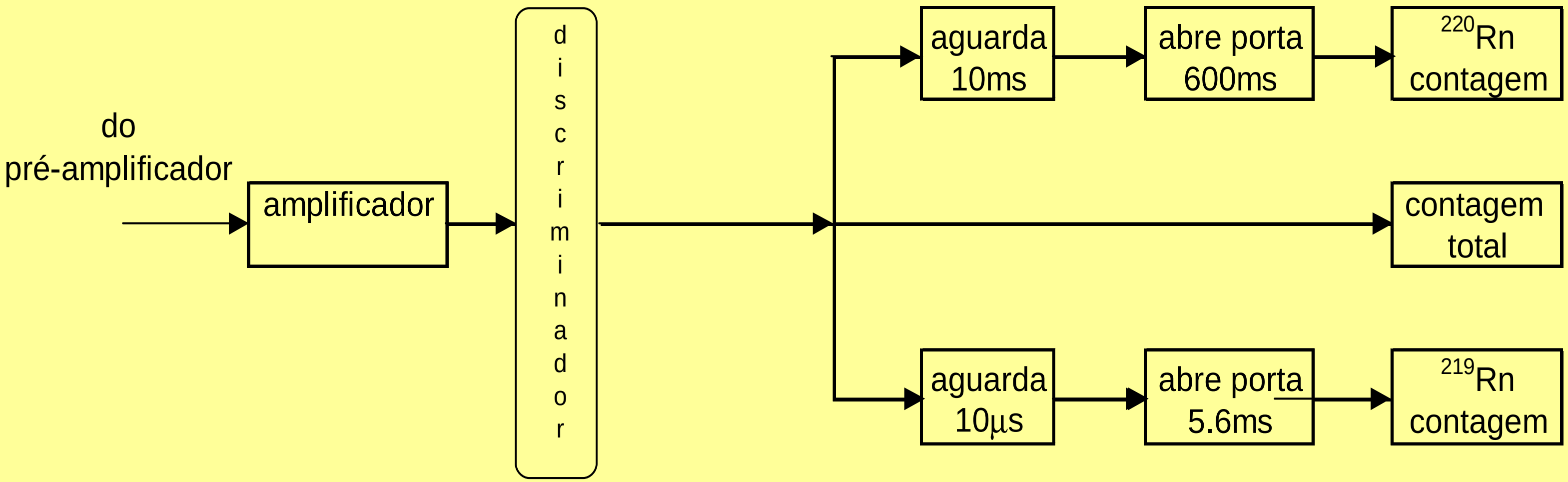
Delayed Coincidence System

$^{224}Ra \rightarrow {}^{220}Rn \rightarrow {}^{216}Po \rightarrow$

$T_{1/2}$ 3.6d 55s 150ms

$^{223}Ra \rightarrow {}^{219}Rn \rightarrow {}^{215}Po \rightarrow$

$T_{1/2}$ 11.4d 4.0 s 1.78ms



Assessment of the cross-shelf Ra distributions in Ubatuba, São Paulo

Residence time and mixing processes of the Ubatuba using Ra isotopes, we report data obtained in three studies carried out in 2000, 2002 and 2003.

All samples studied here were taken in the selected area between latitudes 23°15'S and 25°50'S and longitudes 44°W and 46°W, in order to estimate coastal mixing rates and ground water discharge fluxes.

- Two short-lived radium isotopes ^{223}Ra and ^{224}Ra can be used as tracers to measure the rate of exchange of coastal waters

Case Study: Results from Ubatuba, Brazil

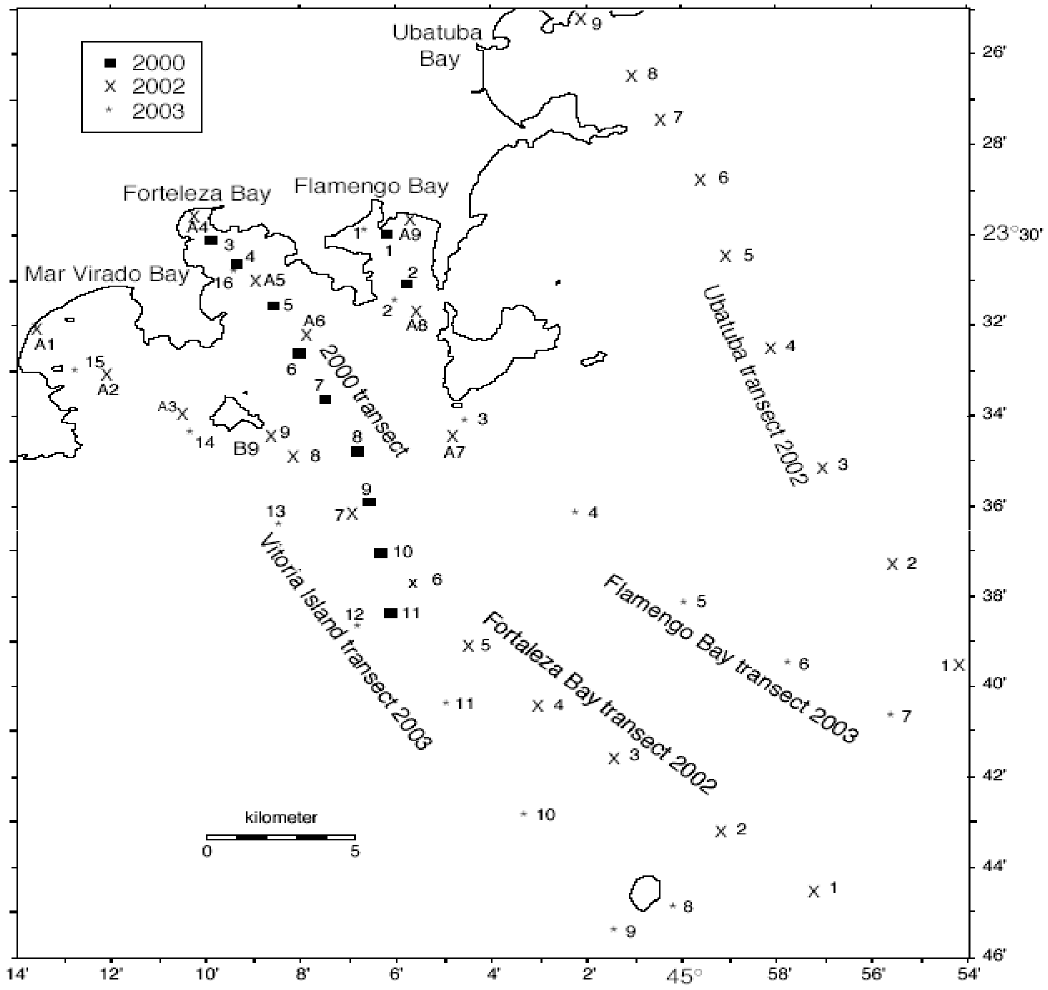


Figure 1. Map of the study area showing cruises conducted in 2000 (squares), 2002 (X) and 2003(*). The offshore transects are labeled. The labels for samples collected in various bays in 2002 have na A prefix.

Results and Discussion

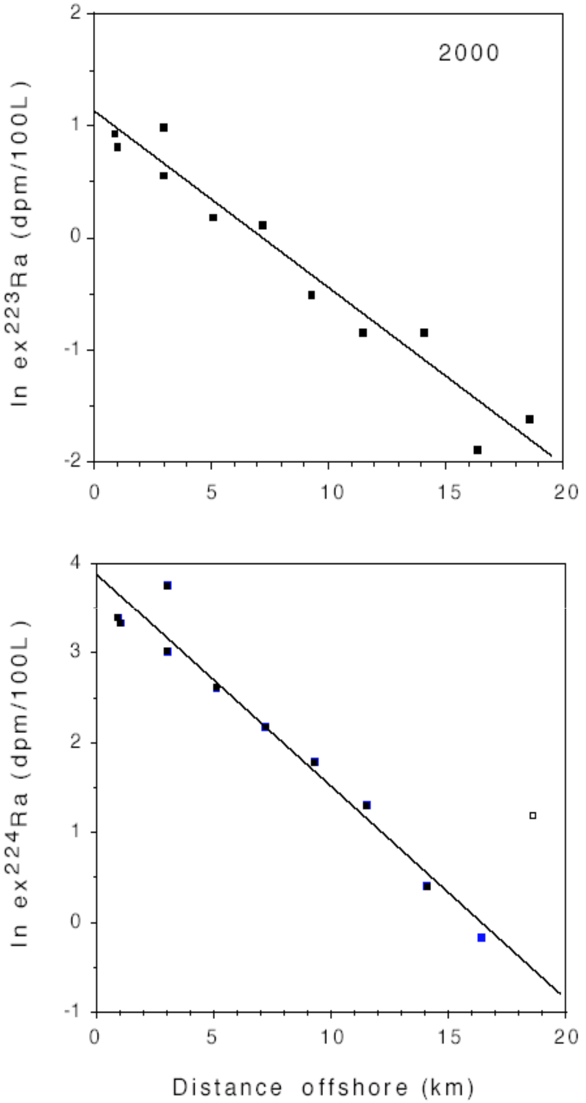


Figure 2. The ln Ra activity as a function of distance offshore for samples collected in 2000. The best fit line for ^{223}Ra (R^2= 0.949) yields K_h = 28 m^2 s^{-1}. The best fit line for ^{224}Ra (R^2= 0.961) yields K_h=30 m^2s^{-1}.

Results and Discussion

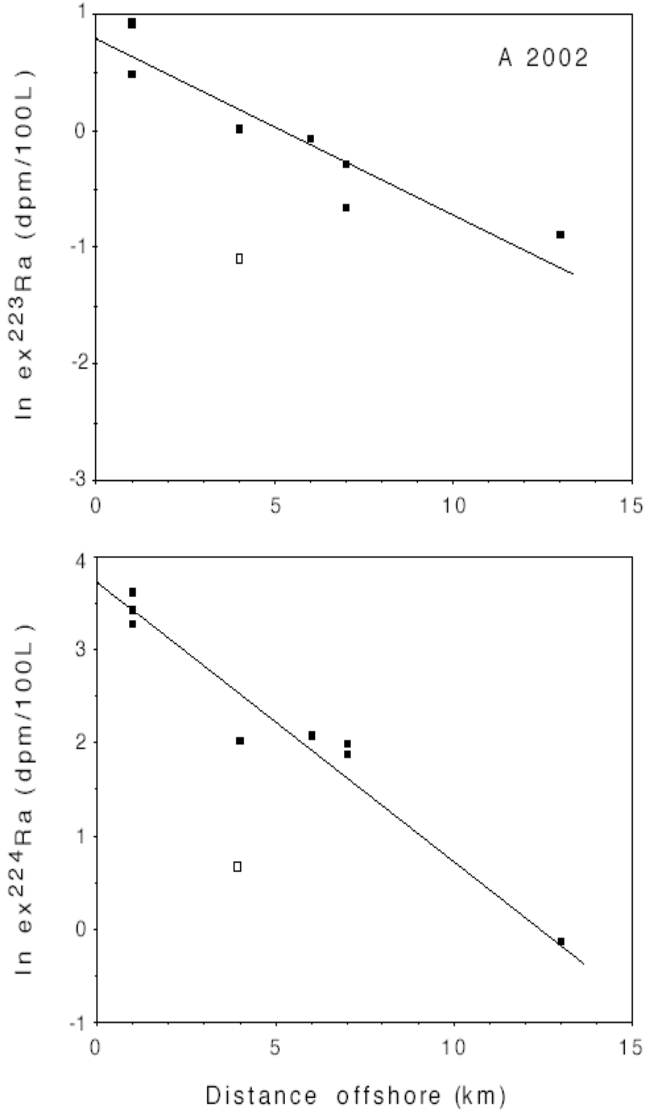


Figure 3. The ln Ra activity as a function of distance offshore for samples collected within 13 km of shore in 2002. The best fit line for ^{223}Ra (R^2= 0.862) yields K_h = 24 m^2 s^{-1}. The best fit line for ^{224}Ra (R^2= 0.950) yields K_h=31 m^2s^{-1}.

Results and Discussion

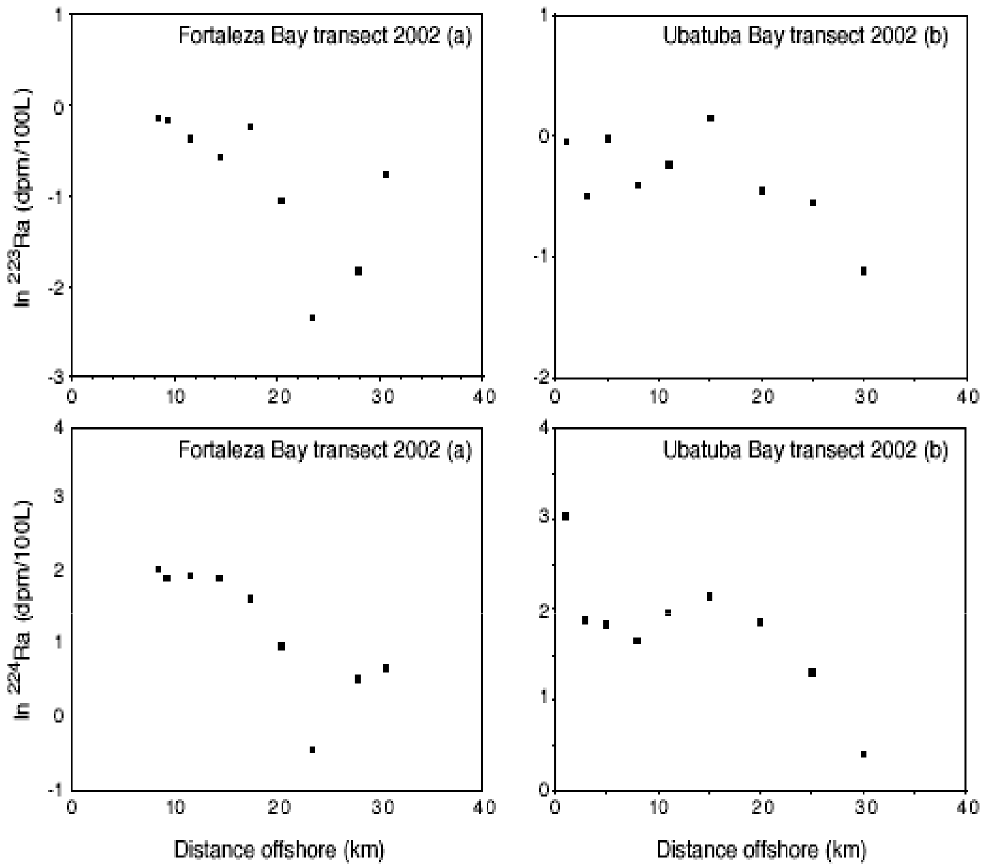


Figure 4. (a) The ln Ra activity as a function of distance offshore for samples collected on the Fortaleza Bay transect in 2002. The ^{223}Ra data are reasonably correlated within 20 km of shore, but the correlation breaks down for samples collected between 20-30 km. (b) The ln Ra activity as a function of distance offshore for samples collected on the Ubatuba Bay transect in 2002. Samples collected within Ubatuba Bay and just shoreward of the bay have activities considerably lower than samples collected from the bays to the south. Additionally, there is no consistent trend of decreasing activity with distance offshore for these samples.

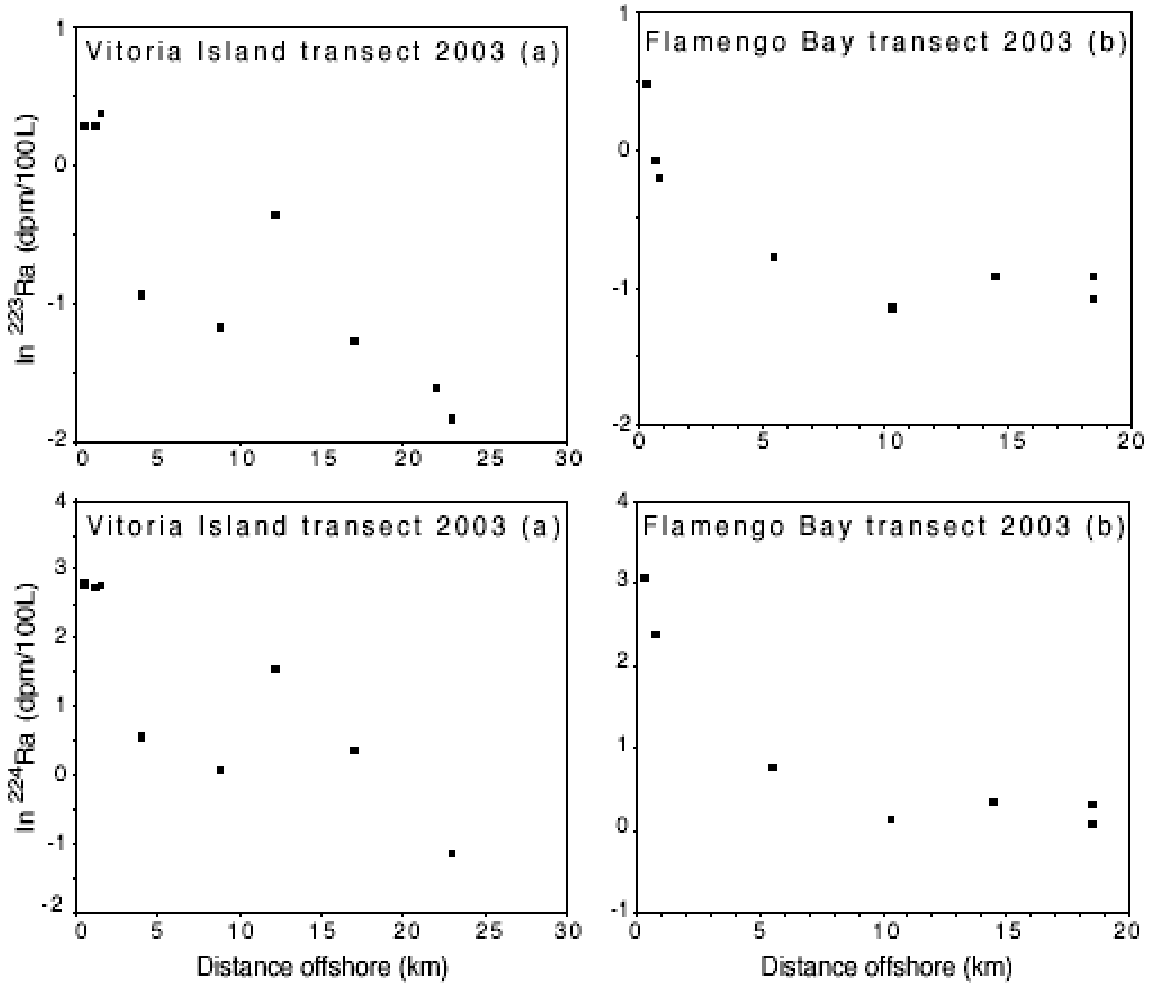


Figure 5. (a) The ln Ra activity as a function of distance offshore for samples collected on the Vitoria Island transect in 2003. There is no consistent trend of decreasing activity with distance offshore for these samples. (b) The ln Ra activity as a function of distance offshore for samples collected on the Flamengo Bay transect in 2003. Samples collected beyond 5 km do not show a decreasing trend of activity with distance.

Results and Discussion

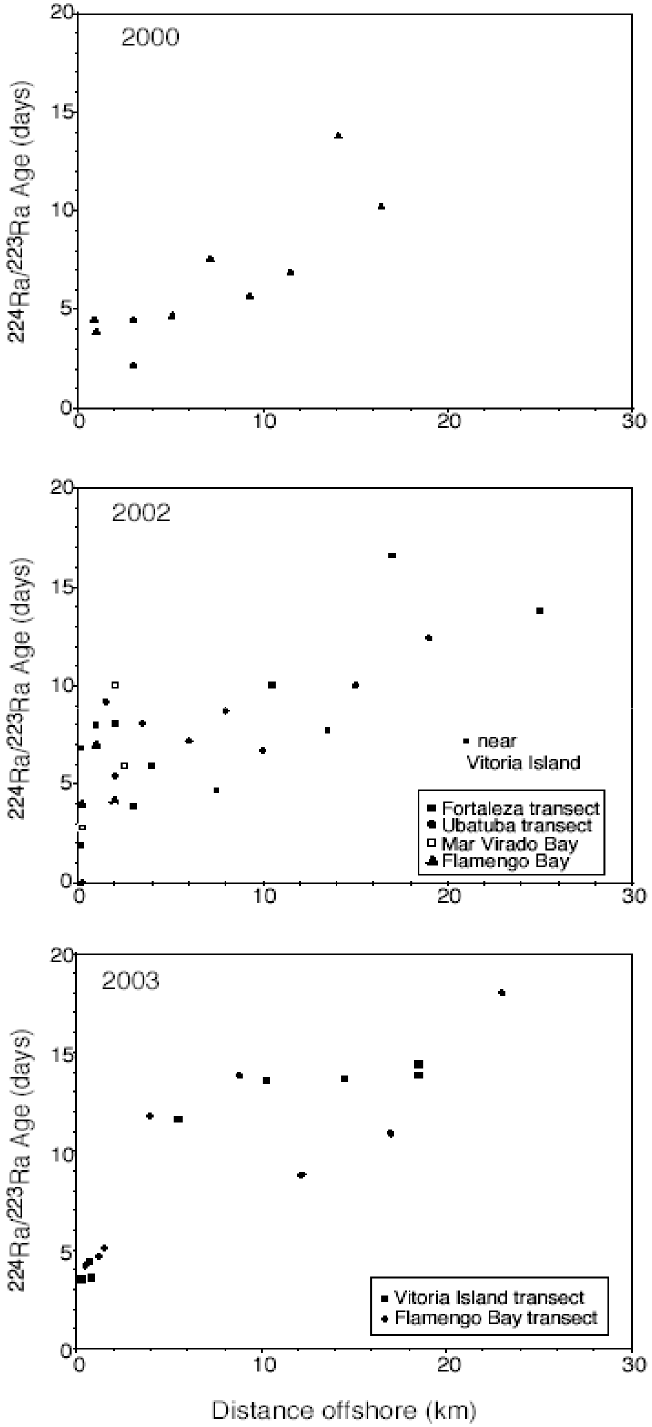


Figure 6. Age vs distance offshore for all samples. Samples collected in the bays have ages in the range of 2-10 days relative to the water collected in the seepage meter. Further offshore there is a trend of increasing age with distance. Most samples from 10-25 km offshore have ages in the range 7-15 days.

The $^{224}Ra/^{223}Ra$ age method provides an estimate of 1-2 weeks for the residence time of water within 25 km of shore.

It ilustrates that the ages do not follow a single trend with distance offshore. This is likely due to the rugged coastline where many bays and small islands interrupt single mixing patterns. As water circulates through these bays, small-scale eddies may develop and propagate onto the shelf. Changes in wind direction must have a strong effect on the eddy formation and circulation.

The likelihood of achieving steady state on a time scale of days to weeks is small.

We used the residence times of the coastal water and the enrichment of ^{228}Ra relative to the ocean to estimate the flux of ^{228}Ra necessary to maintain this enrichment.

Our results indicate that the nearshore (0-50 m) SGD flux could only support 10% of the measured ^{228}Ra enrichment. This implies that there is considerable offshore SGD.

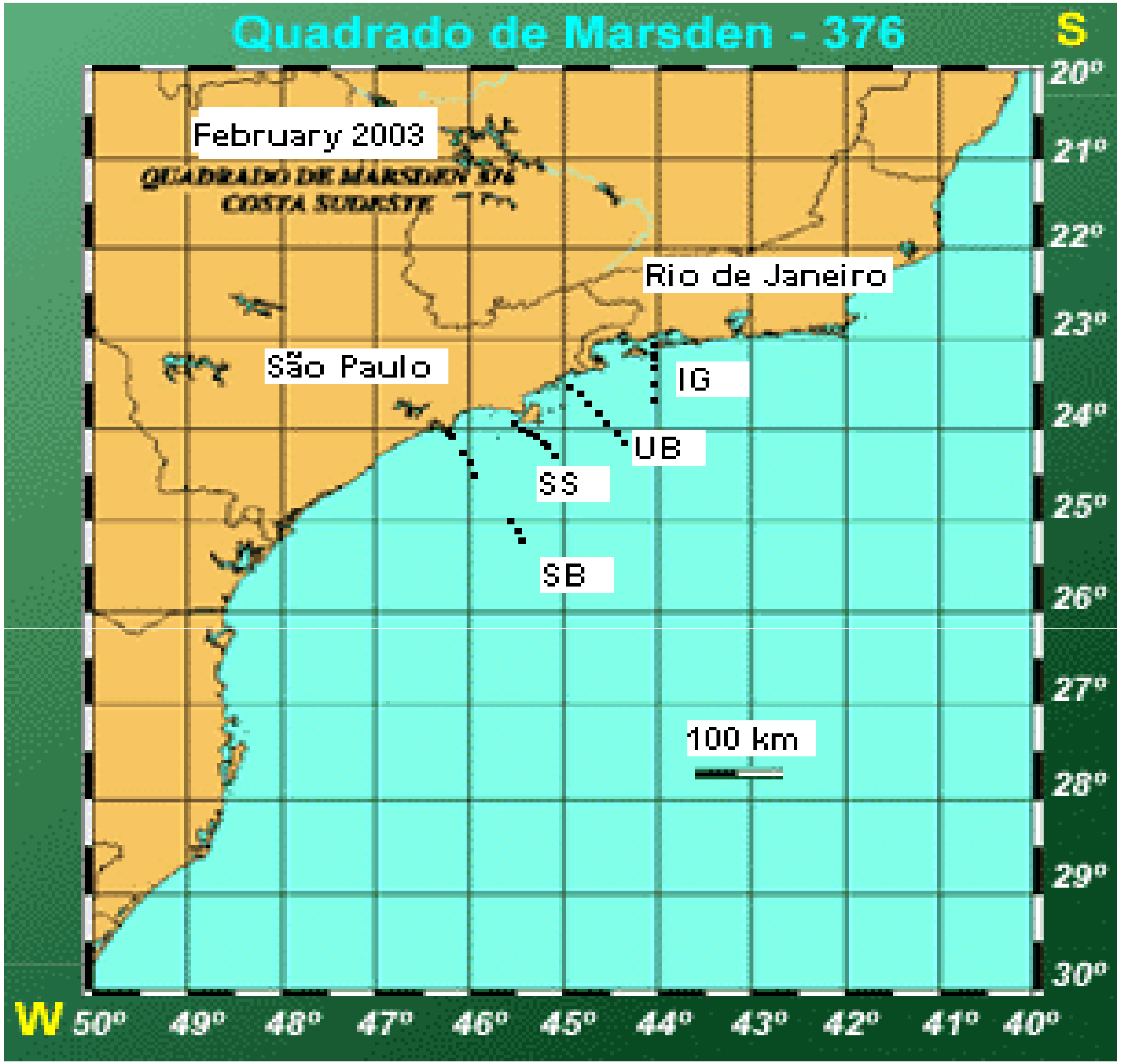
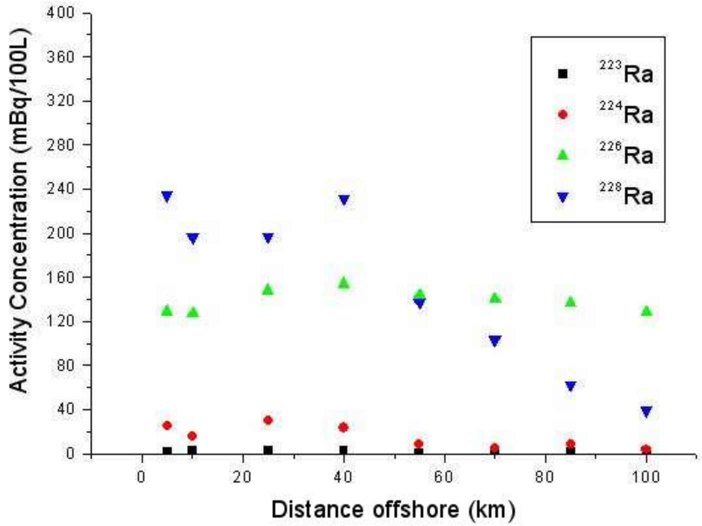
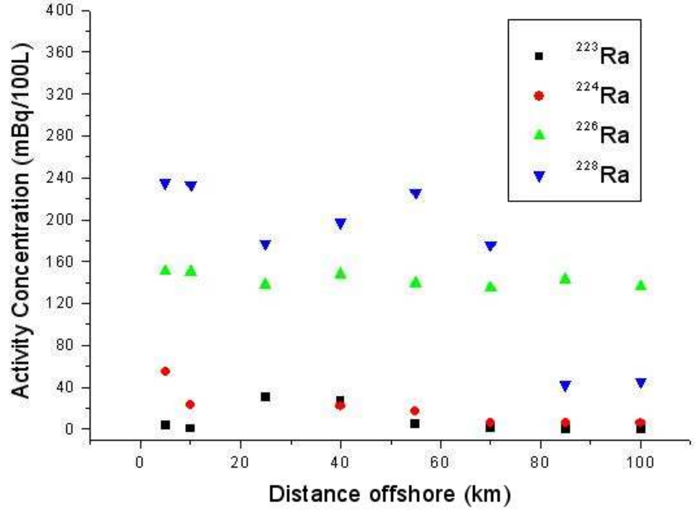


Figure 7. Sampling performed at São Paulo Bight. IG – horizontal profile Ilha Grande, UB-Ubatuba, SS-São Sebastião and SB-Santos.

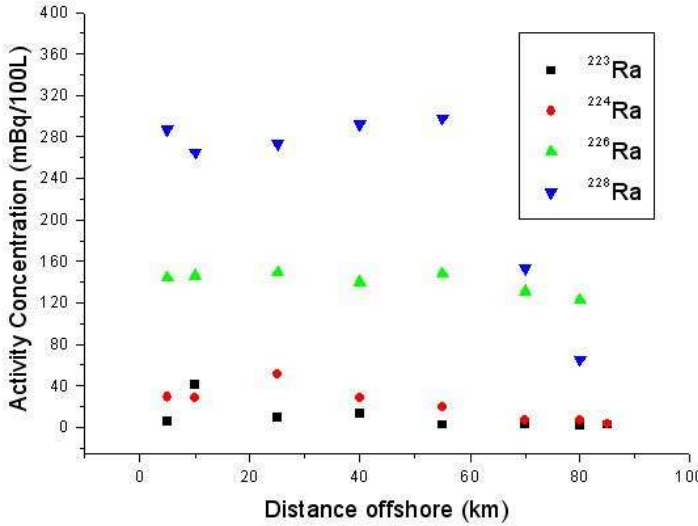
Ra distributions



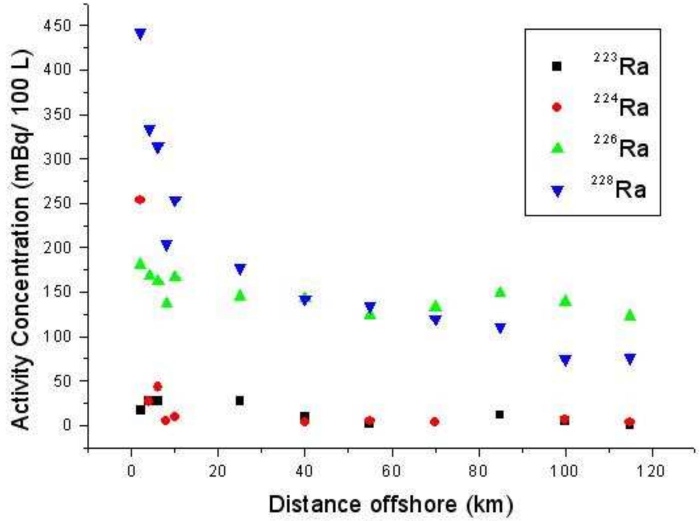
Ilha Grande Transect



Ubatuba Transect

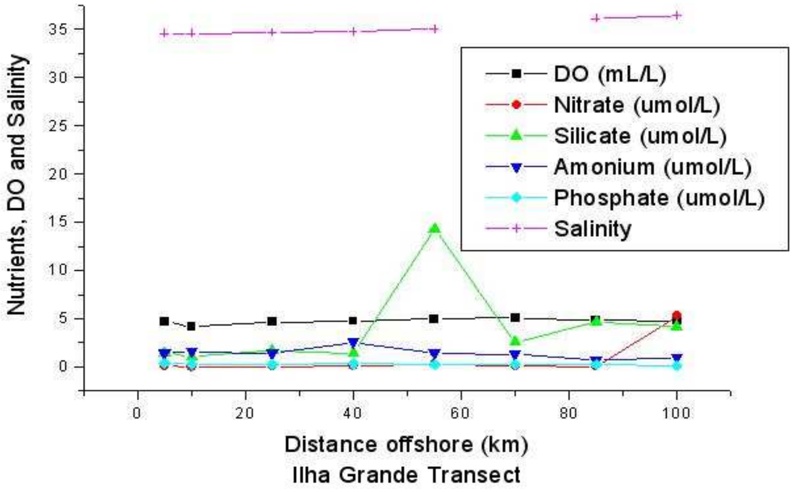


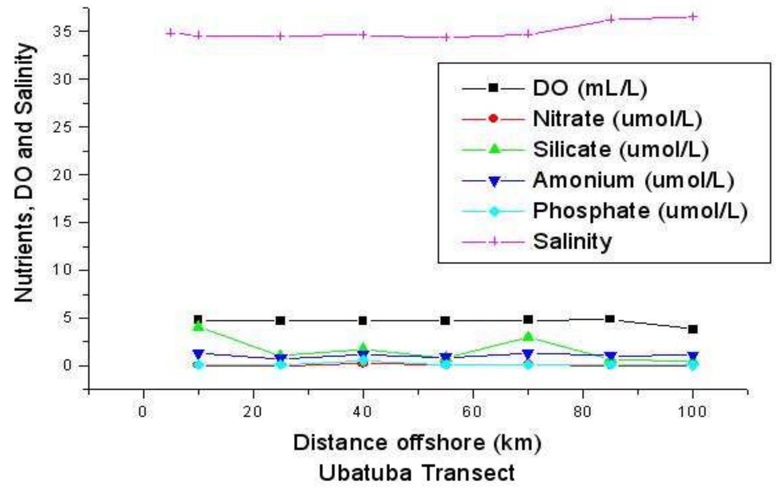
São Sebastião Transect

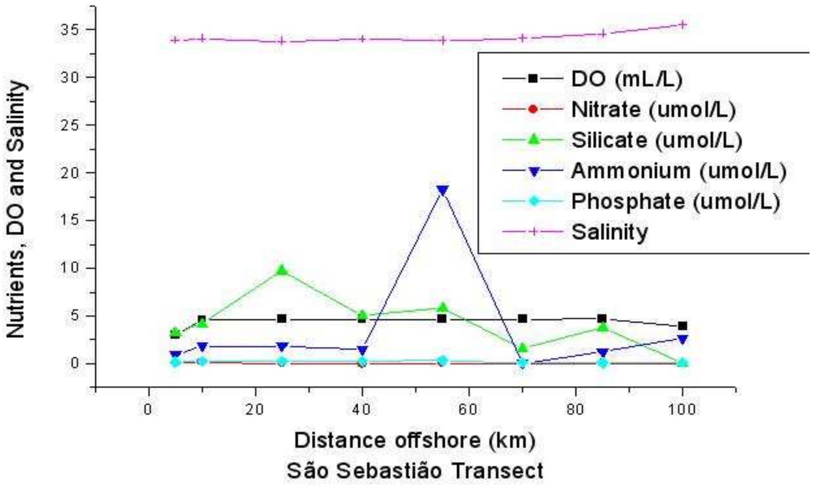


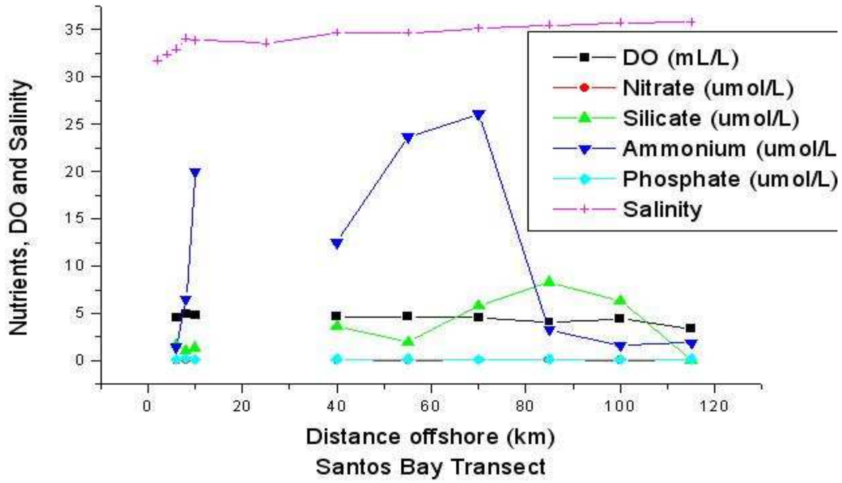
Santos Bay transect

DO, nutrients and salinity

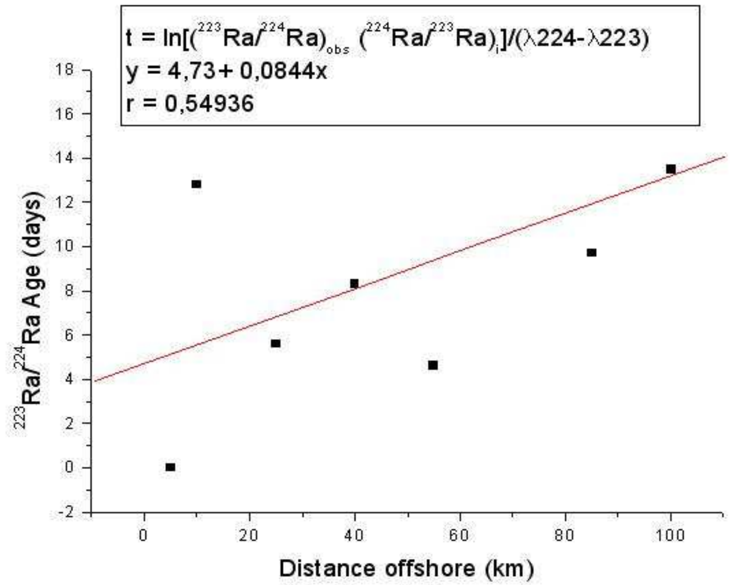




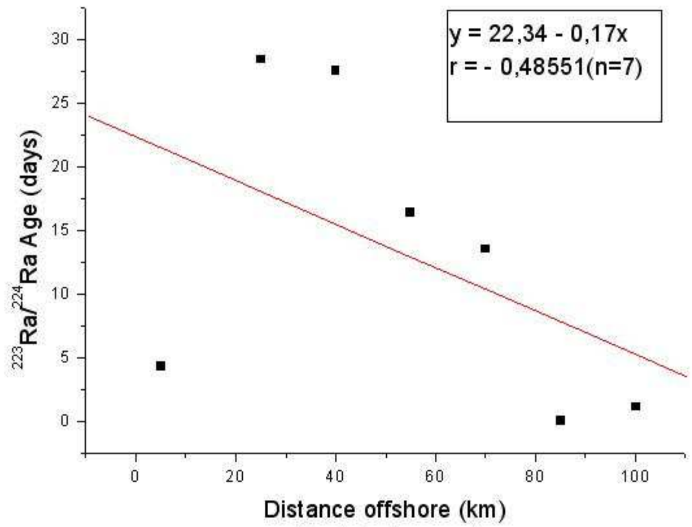




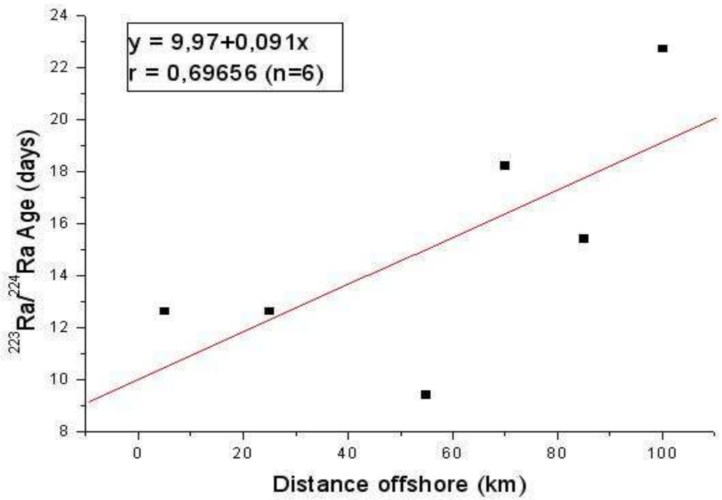
Aparent ages of water masses $^{223}Ra/^{224}Ra$



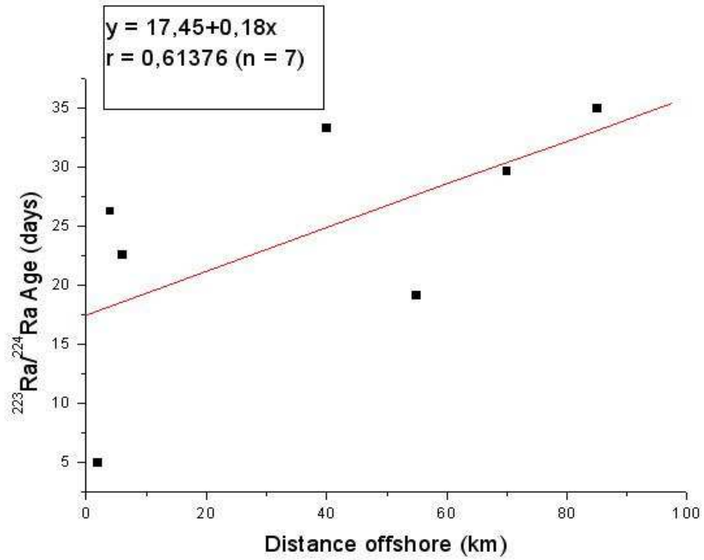
Ilha Grande Transect



Ubatuba transect

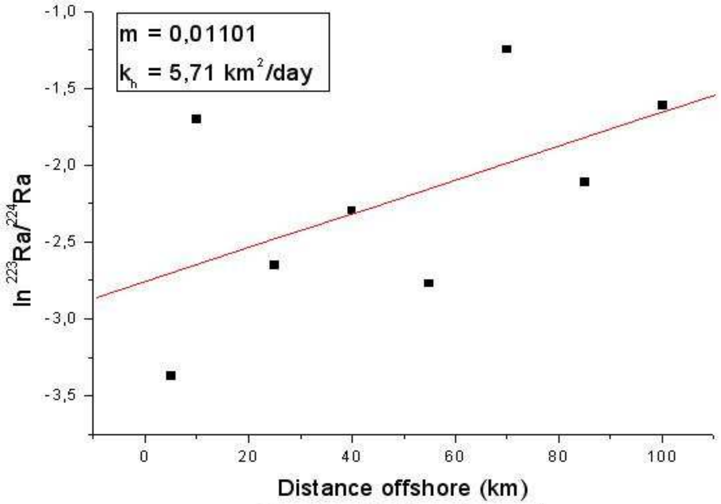


São Sebastião Transect



Santos Bay Transect

Mixing coeficients (K_h)



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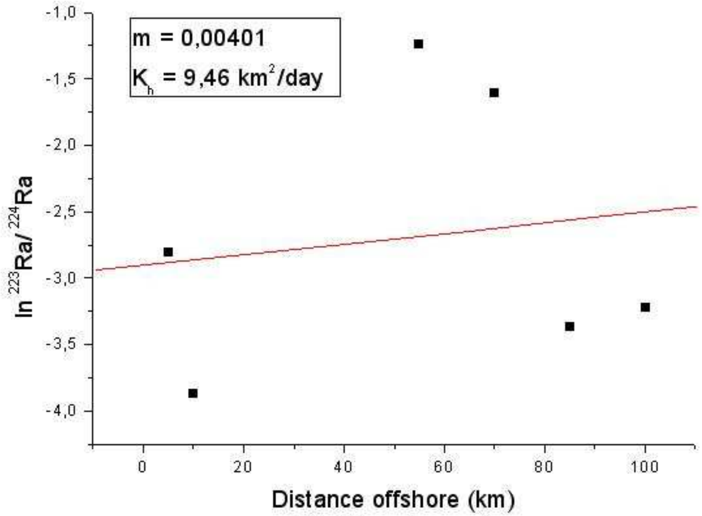
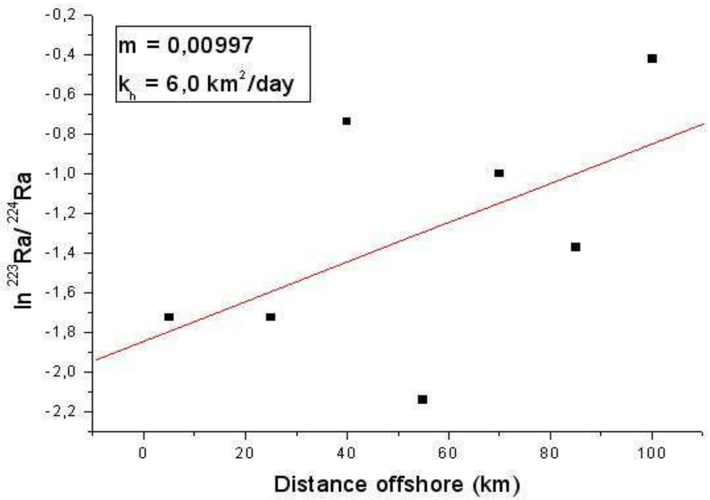


Ubatuba Transect



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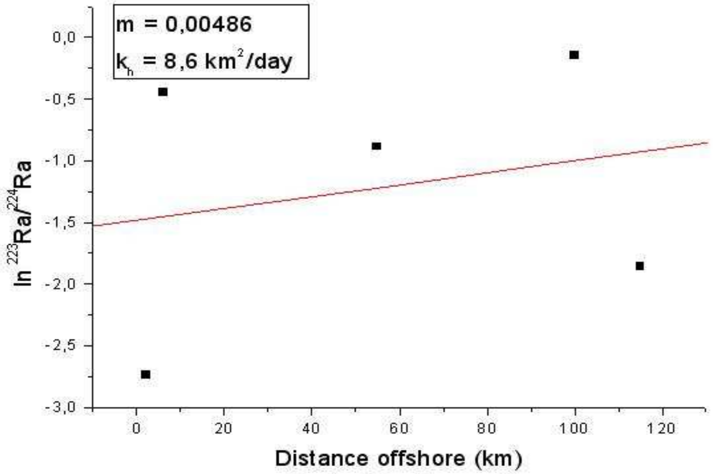


Santos Bay Transect

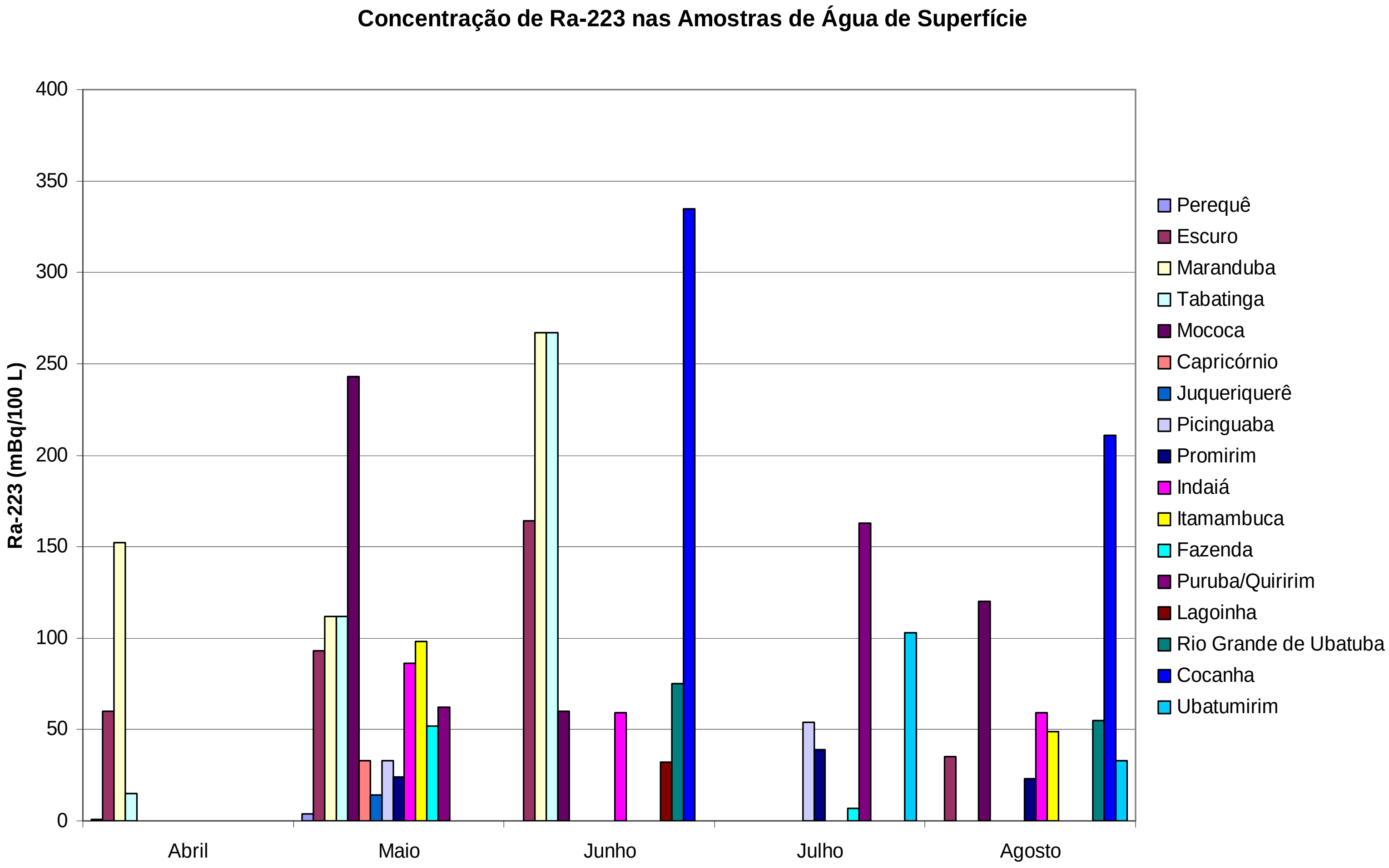
IG profile ages varied from 4 days (distance zero) to 14 days (100 km offshore).

SS profile from 9 to 20 days.

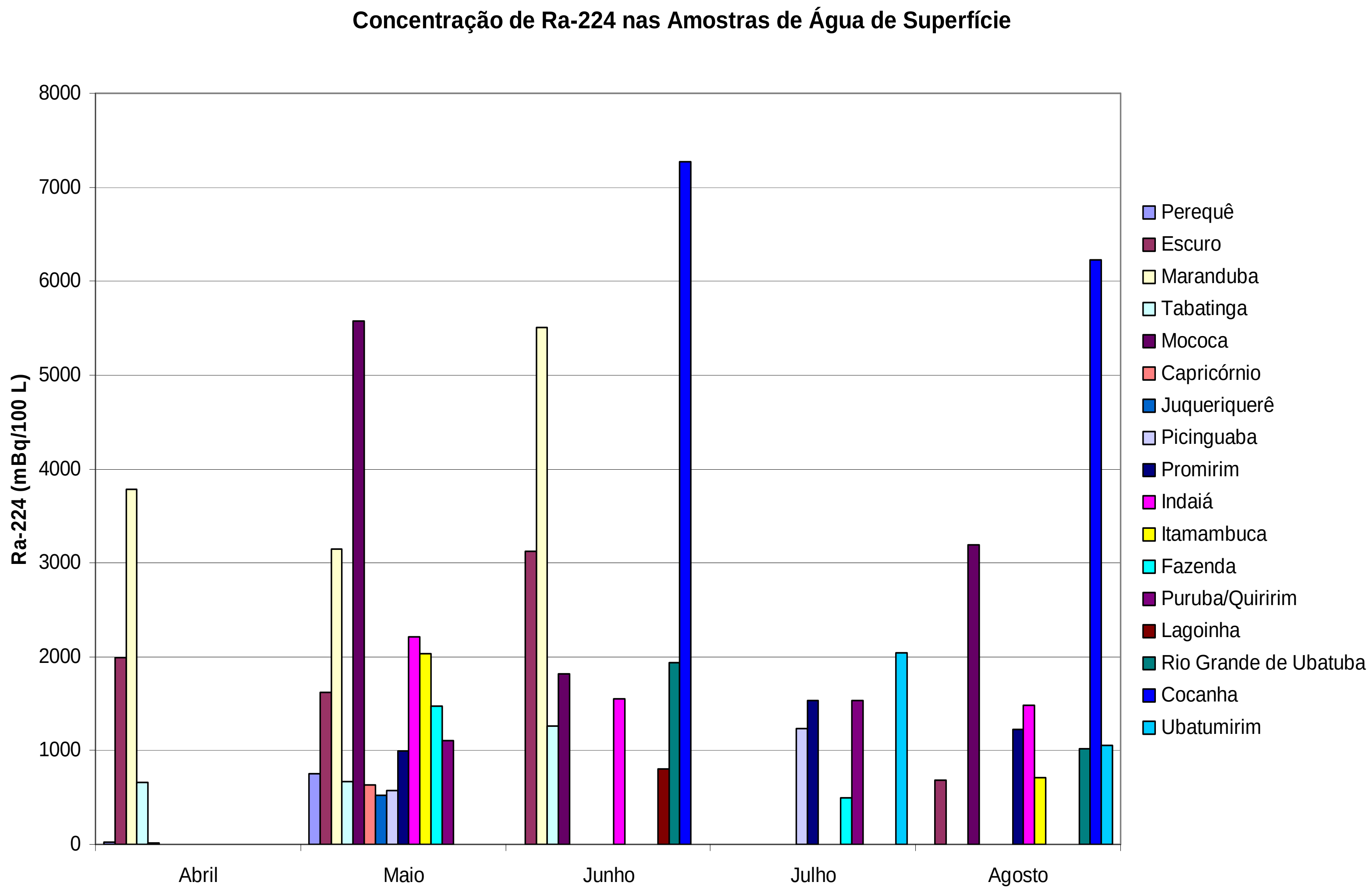
SB profile from 17 to 35 days.

Average exchange rates of 23 days, during the period of investigation.

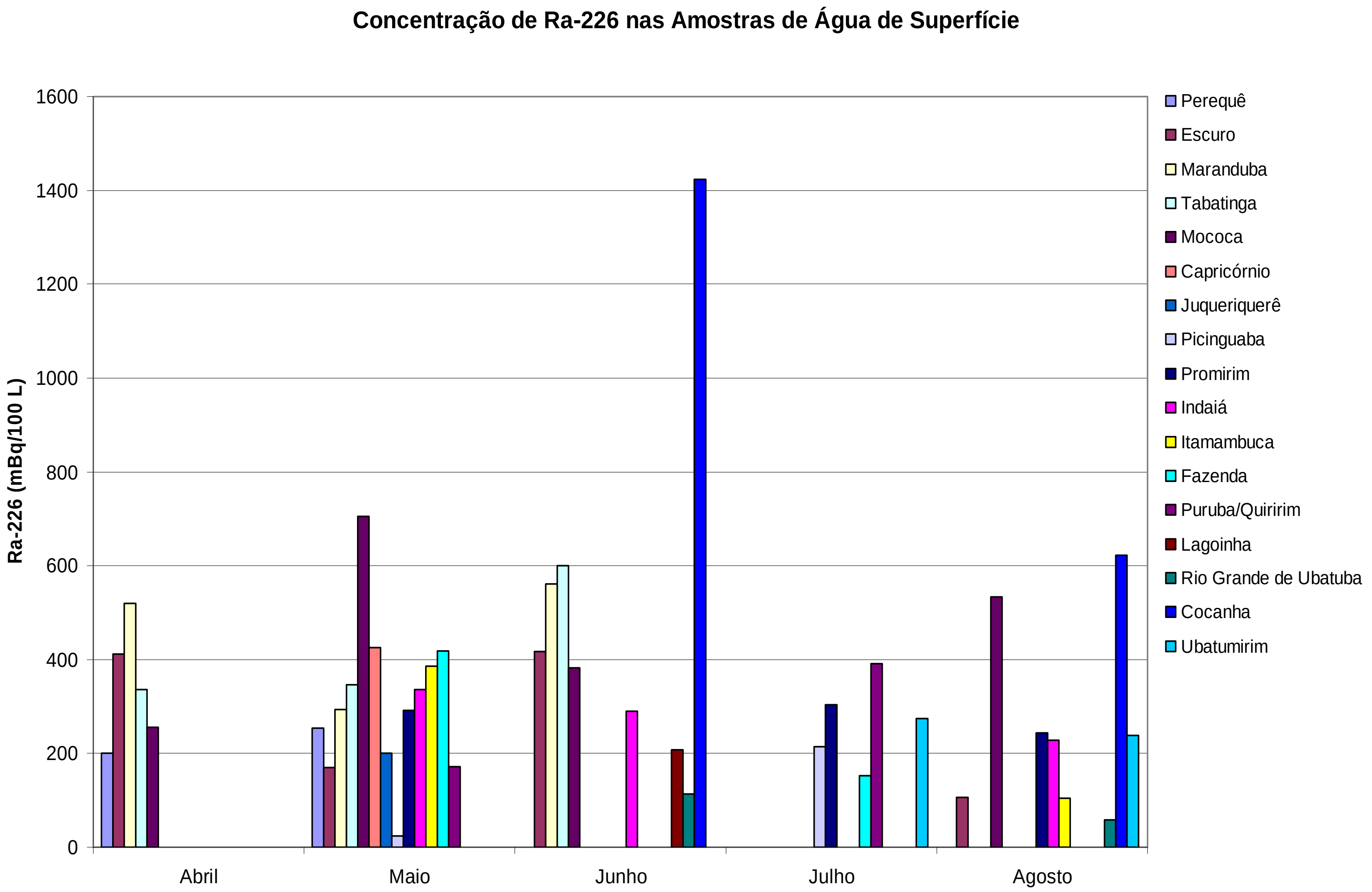
Ra distributions river water Ubatuba



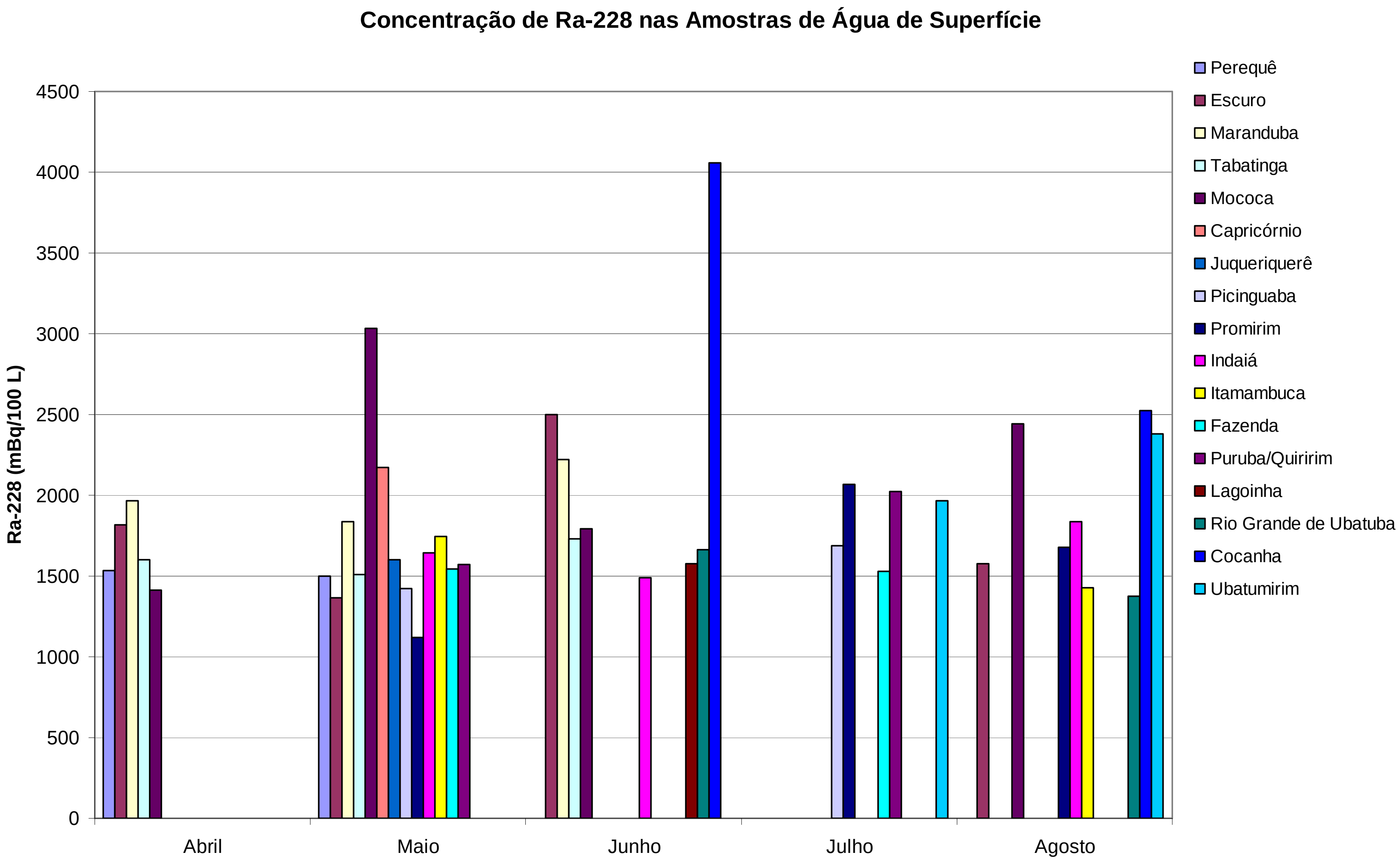
Distribuição das concentrações de atividade de ^{223}Ra em todos os rios estudados de Abril a Agosto de 2007.



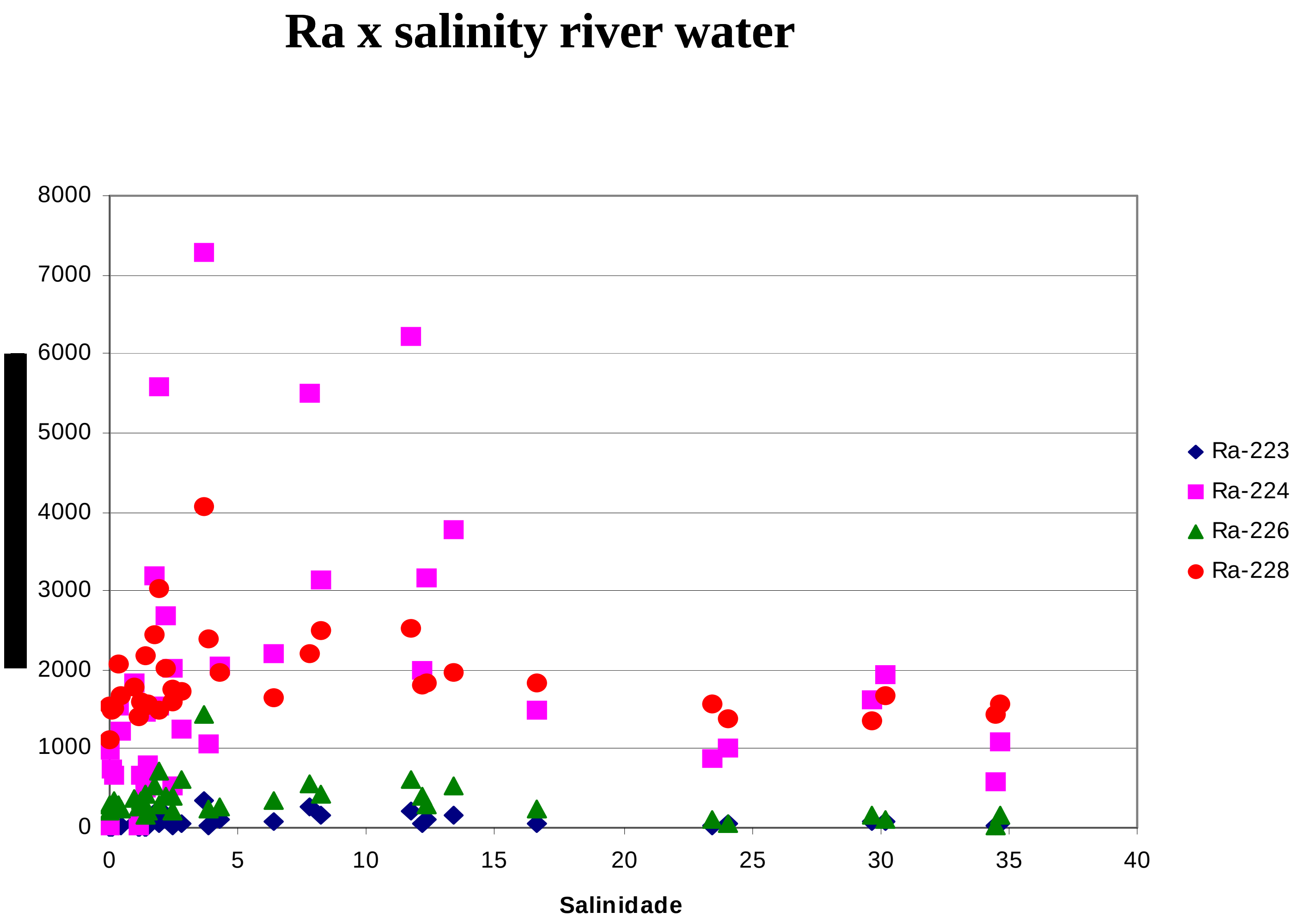
Distribuição das concentrações de atividade de ^{224}Ra em todos os rios estudados de Abril a Agosto de 2007.



Distribuição das concentrações de atividade de ^{226}Ra em todos os rios estudados de Abril a Agosto de 2007.

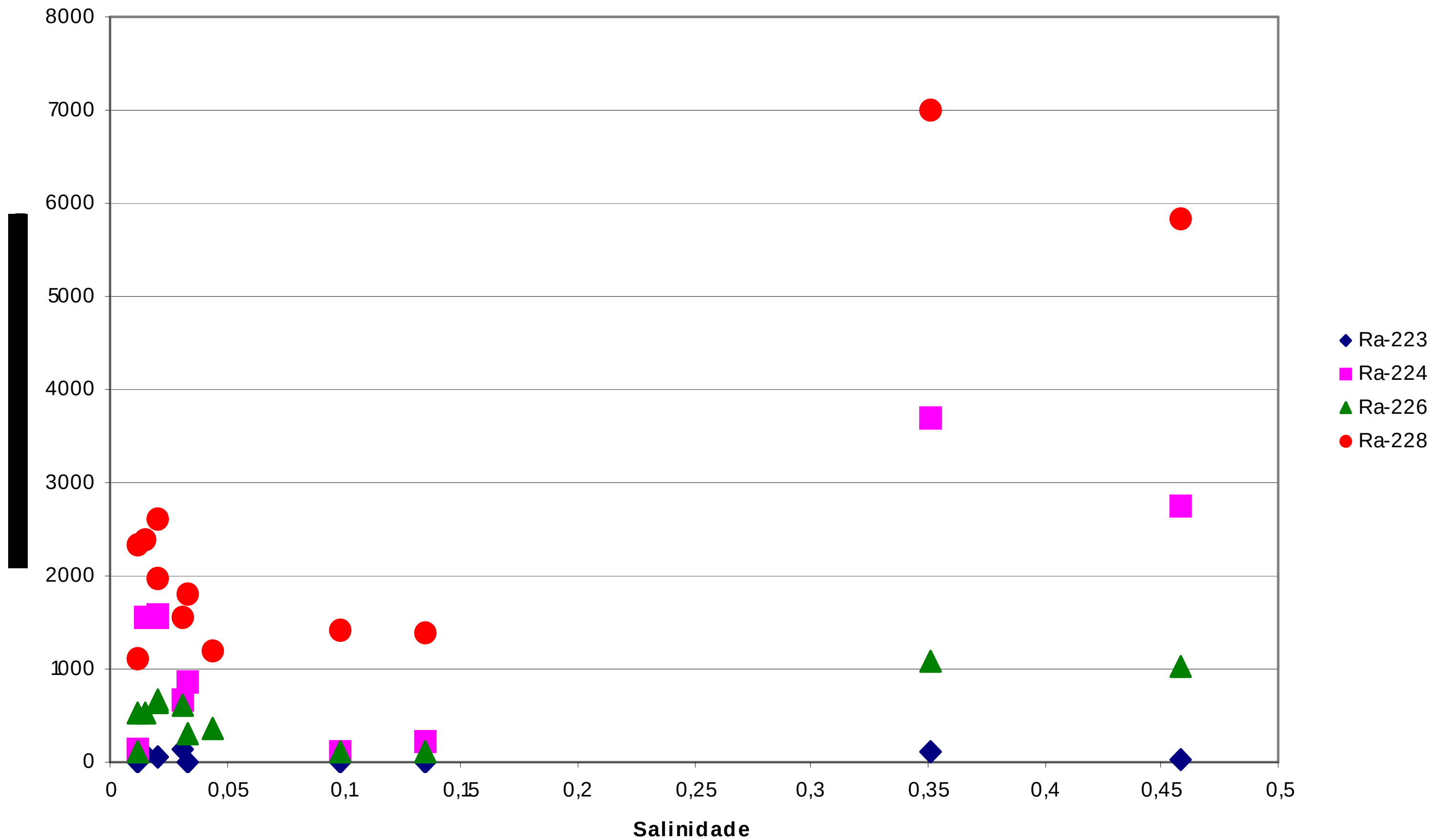


Distribuição das concentrações de atividade de ^{228}Ra em todos os rios estudados de Abril a Agosto de 2007.



Distribuição das concentrações dos isótopos naturais em função da salinidade observada nas amostras de água dos rios.

Ra x salinity groundwater



Distribuição das concentrações dos isótopos naturais de Ra em função da salinidade observada nas amostras de água subterrânea.

The average fluvial fluxes of ^{226}Ra, ^{228}Ra and dissolved Ba were estimated in this work assuming the steady-state condition and neglecting changes in volume due to evaporation and precipitation processes.

The following derived equation describes simultaneously the volume conservation (Q), salinity (S) and concentration of a conservative element (C):

$$C_R + \frac{I_C}{Q_R} = \left(\frac{S_0}{S_0 - S_E} \right) C_E - \left(\frac{S_E}{S_0 - S_E} \right) C_0$$

For these calculations the following average values were used:
C_R= average riverine input of ^{226}Ra (3440 mBq m^{-3}), ^{228}Ra (17480 mBq m^{-3}) and dissolved Ba (4.4 g m^{-3}) from April to June 2007 for Ubatuba embayments.
Q_R = total discharging volume of all rivers studied (105 m^3 s^{-1}); in a total drainage area of 1977 km^2 .
S_O = 34.6 (this work)
S_E = 30.6.
C_O = average concentrations of ^{226}Ra (1500 mBq m^{-3}), ^{228}Ra (4090 mBq m^{-3}), Ba (4.1 g m^{-3}) in oceanic waters.
C_E = average concentrations of ^{226}Ra (2300 mBq m^{-3}), ^{228}Ra (7450 mBq m^{-3}), Ba (5.5 g m^{-3}) in estuarine waters .

Conservative Element	Ic (g m^{-3} and/ or Bq m^{-3})
^{226}Ra	553
^{228}Ra	1646
Dissolved Barium	1240

Cananéia-Iguape

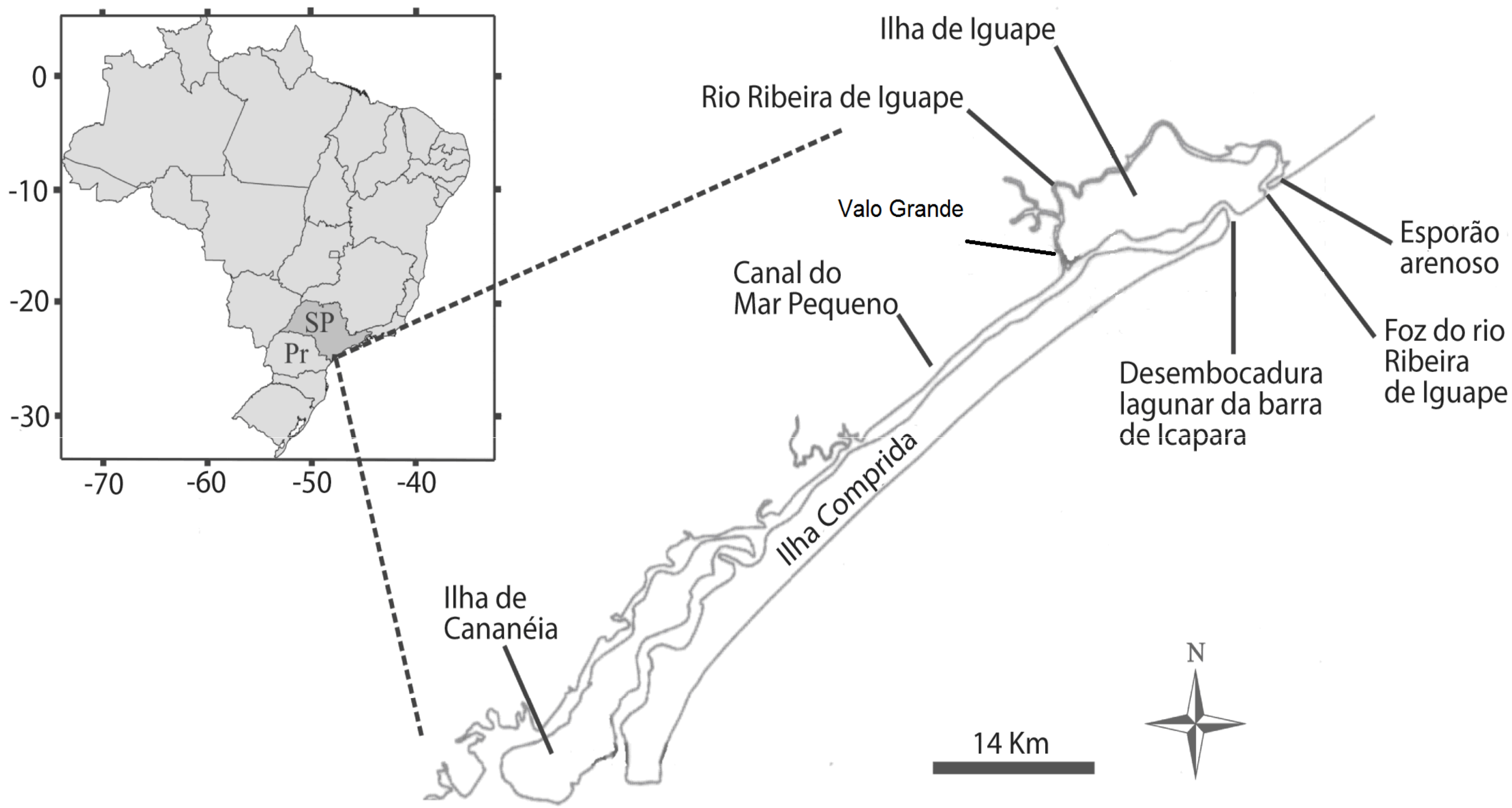


FIGURA 3- Localização do sistema estuarino Cananéia-Iguape.

Sampling

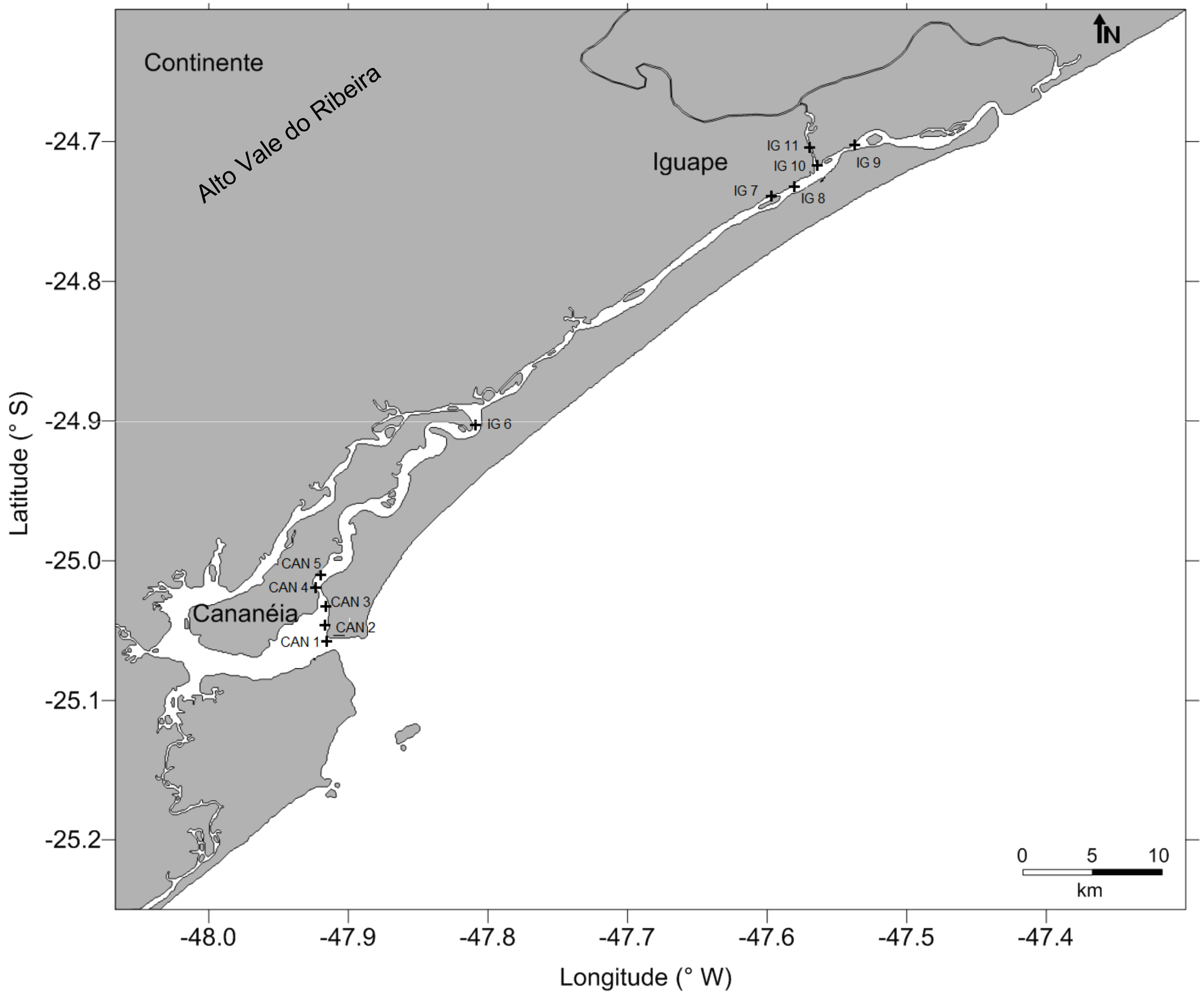


FIGURA 4- Localização das estações hidroquímicas no sistema estuarino Cananéia-Iguape.


Cananéia


Iguape


Rio Ribeira de Iguape

The distribution of natural Ra isotopes was studied in surface, groundwater and estuarine water samples collected from dry and wet seasons (2009 – 2010) campaigns performed in Ribeira Valley, Southern São Paulo State.

The inventory allowed the application of Ra isotopes as tracers of groundwater/ surface water in Ribeira do Iguape River basin and related fluxes of several constituents for the Cananéia-Iguape estuarine complex.

The results obtained in this research work evidenced that there is a prevalence of ^{228}Ra isotope in all the set of samples analyzed.

The activity concentrations of Ra isotopes determined from Higher Ribeira Valley through the Southern Coastal Plain of São Paulo are representative of natural background levels, showing low or minimal human intervention.

In the set of samples collected along Ribeira do Iguape River, Cananéia and Iguape outlets, the higher concentrations of Ra were observed in bottom waters, indicating the diffusion of ^{228}Ra from sediments recently deposited as a potential source of the increased concentrations of this isotope when compared with others.

The activity concentrations of the short-lived Ra isotopes were negligible, lower than the limit of the detection.

Fluxes of Ra for Cananéia outlet are strongly influenced by tidal oscillations, which modulate the increase and decrease of Ra concentrations in response of the respective increase and decrease of waters salinity.

In Iguape outlet and in hydrochemical stations performed along Ribeira do Iguape River it was observed a linear relationship between the amount of suspended matter and the increase of ^{228}Ra activity concentration.

When we evaluate qualitatively the differences in behavior of both long-lived Ra isotopes, the concentrations of ^{226}Ra have not shown similar distribution to ^{228}Ra. This demonstrates negligible contribution from advective porewaters and groundwater to the studied scenario. Dominant fluxes of trace-elements, radionuclides and nutrients have their main sources centered on fluvial, sediments and suspended matter compartiments.