

# Passive biomonitoring study for trace elements in oysters *Crassostrea brasiliensis* (Lamarck, 1819: Mollusca, Bivalvia) in São Paulo State coastal sites, Brazil (25°00'-23°56'S, 47°25'-45°19'W)

M. G. M. Catharino<sup>1</sup>, M. B. A. Vasconcellos<sup>1</sup>, A. A. Kirschbaum<sup>2</sup>, M. R. Gasparro<sup>2</sup>, E. C. P. M. de Sousa<sup>2</sup>, C. C. Minei<sup>2</sup>, E. G. Moreira<sup>1</sup>, D. Seo<sup>1</sup>



<sup>1</sup> Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, São Paulo, SP, 05508-000, Brazil - [mgcatharino@uol.com.br](mailto:mgcatharino@uol.com.br)

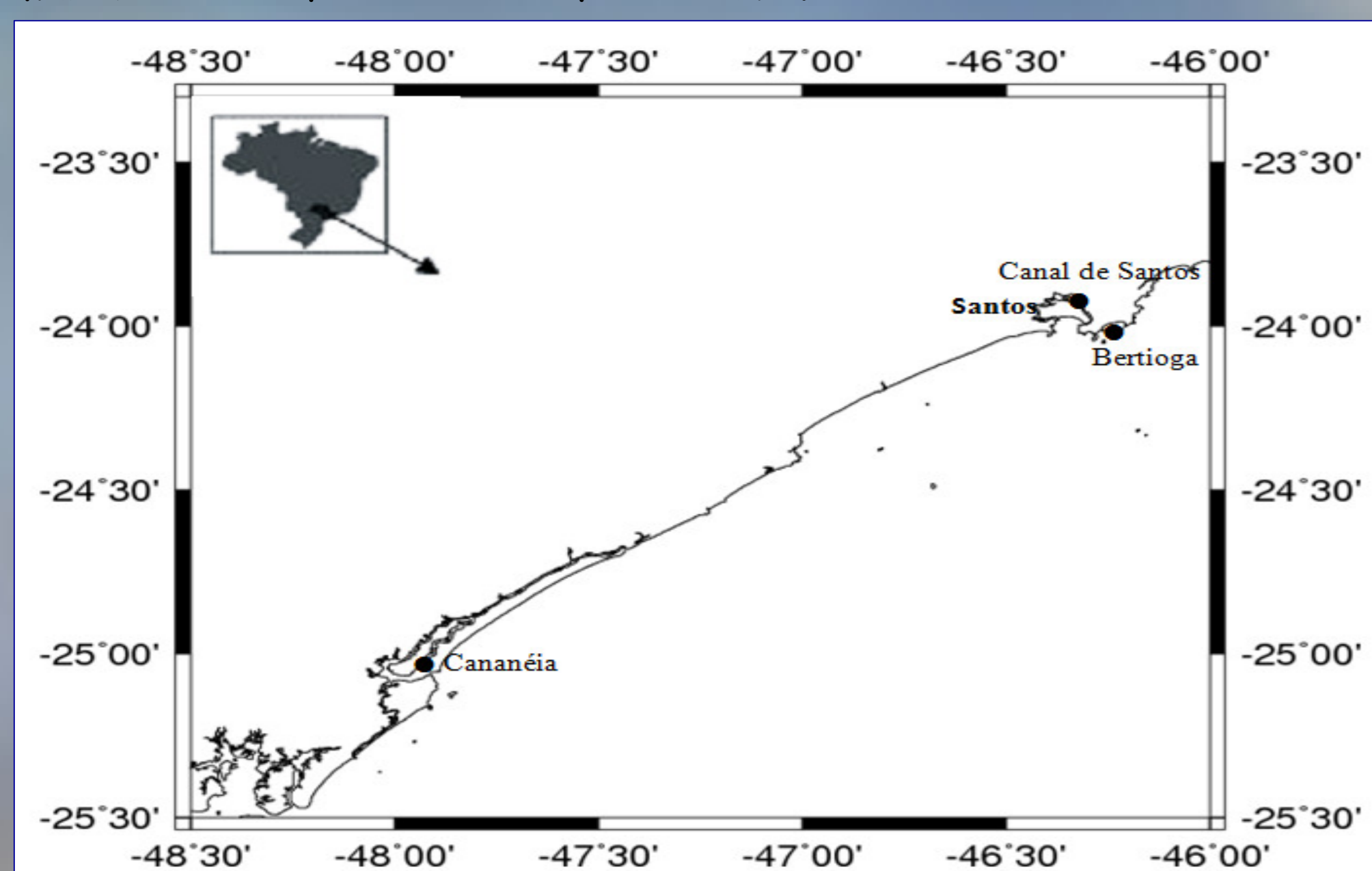
<sup>2</sup> Laboratório de Ecotoxicologia Marinha e Microfitobentos, Instituto Oceanográfico da Universidade de São Paulo, IOUSP, Praça do Oceanográfico, 191, Cidade Universitária, São Paulo, SP, 05508-120, Brazil

## INTRODUCTION

Estuaries are highly dynamic environments with physical, chemical and biological structures characterized by high spatial and temporal variability. The temporal fluctuations and spatial gradients in these systems induce large variability in chemical and biological properties of the water and sediment. The estuaries are very often heavily utilized and impacted by mankind, being used as natural harbours, for fish farming, for recreation and waste water recipient. Presently, about 60% of the world's population live along the estuaries and coast. A direct consequence of human occupation of these coastal areas is that estuaries rank among the environments most impacted by human activities. In this study two estuarine areas were chosen: Santos Estuary, one of the most polluted in the world and Cananéia Estuary, one of the most preserved in the coast of São Paulo State.

### Study Area

The above figure shows the study area, located at region of the marine coast of the State of São Paulo.



### Collection of Oyster Samples

Oysters *C. brasiliensis* were collected at three areas, seasonally between September/2008 and July/2009:

- Cananéia Estuary (oyster farm, reference site),
- Bertioga and Canal de Santos - Santos Estuary (impacted by industrial and urban activities in moderate and heavy levels, respectively)

### Analysis

- INAA was employed to measure As, Co, Cr, Fe, Se and Zn.
- (CV AAS) was employed to measure Hg.
- (ET AAS) was employed to measure Cd and Pb.

### Oyster *Crassostrea brasiliensis*



### Certified Reference Material (SRM)

In order to evaluate the quality of the analytical results, the reference material NIST SRM 1566b Oyster Tissue was analyzed along with samples.

### Sample Preparation

Selected 90 organisms from each point and season of the year

- Tissue removal of the shells
- Homogenization of samples
- Weighing of samples
- Lyophilization
- Crushing
- Sieving

### Statistical Analysis

The elements concentrations obtained were evaluated by one-way analysis of variance (ANOVA) and Tukey test ( $p < 0.05$ ) using Bioestat 5.0.

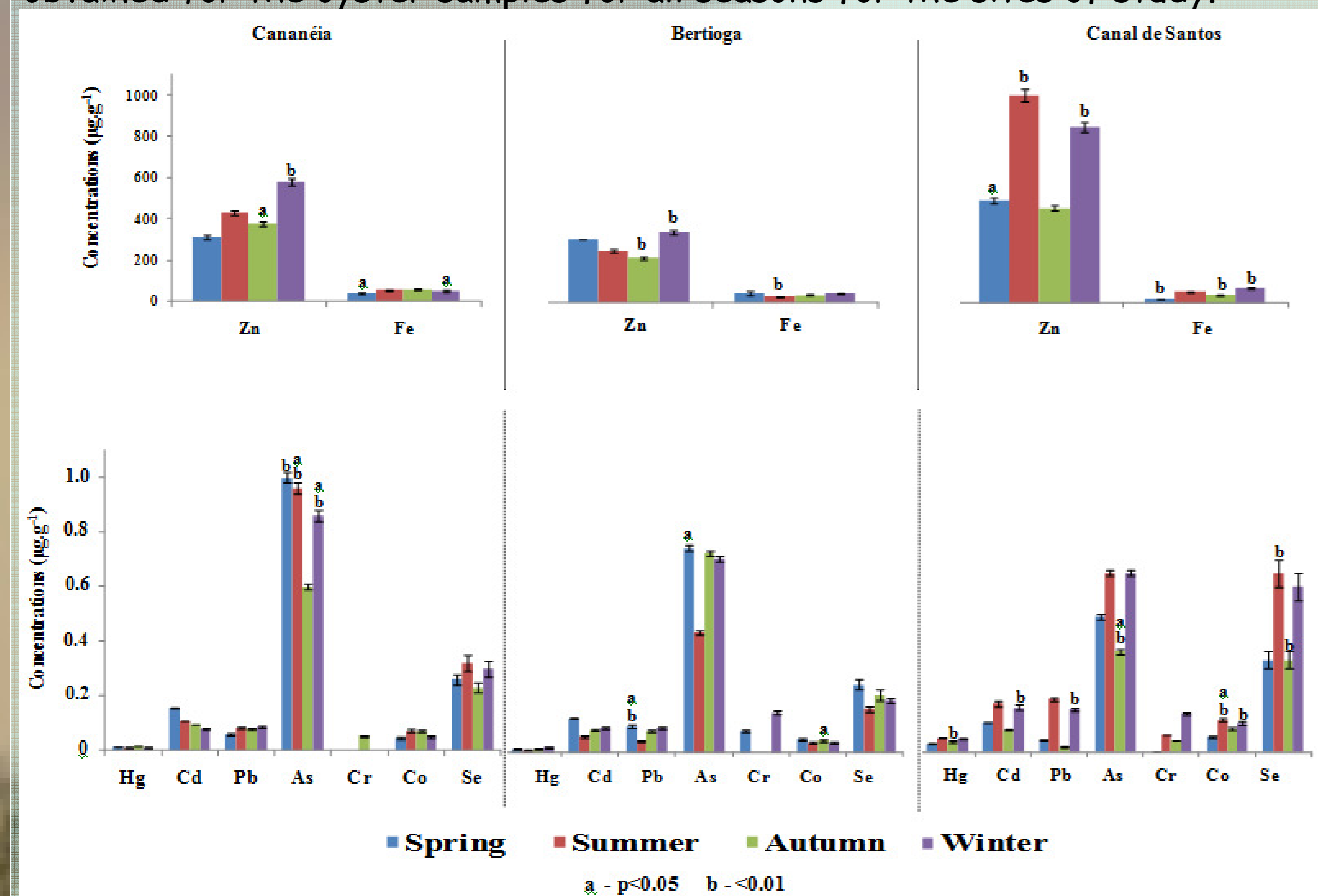
## RESULTS AND DISCUSSION

### Reference Materials

The relative errors obtained ranged from 1.9 to 8.2%. The z-scores  $< 3$ .

### Oyster Samples

This figure present a summary of means and uncertainties of the results obtained for the oyster samples for all seasons for the sites of study.



### Tolerance Limits

#### Brazilian Regulations for Human Consumption of Oyster

The Hg, Cd and Pb did not exceed the limits (0.5, 1.0, 2.0 mg.g<sup>-1</sup>, respectively).

In Cananéia (Springtime) the As was the same of the tolerance limit of 1.0 mg.g<sup>-1</sup>.

For Cr, only Bertioga and Canal de Santos (Winter) were above the limit of tolerance (0.10 mg.g<sup>-1</sup>).

The Se were above the limit of 0.30 mg.g<sup>-1</sup> in Cananéia (Summer and Winter) and in all seasons in the Canal de Santos.

In all sites and seasons the concentrations of Zn were about 4 times greater than the value established.

The element Fe has no limits in the Brazilian legislation.

### Acknowledgements

The authors would like to acknowledge the financial support from FAPESP (Research Project 2011/12240-0), from Brazil and IAEA from Vienna.

### Comparison Between Sites

- In most cases, high concentrations of the elements were detected in the Canal de Santos, except for the element As. There were significant differences ( $p < 0.05$ ) in Cd, Pb, Co and Fe in Winter, Co, Se, Fe and Zn in Summer, Hg, Se, Co, Fe and Zn in Autumn. The high concentrations of these elements may be attributed to the numerous effluents discharged by local industries, the Port of Santos, the vessels that circulate through there, and the dredging of sediment that occurs often.
- In Bertioga site the concentrations were higher for the elements Pb (Spring and Autumn), As (Autumn), Cr and Fe (Spring), with significant differences only for Pb and Fe in the Spring and As in the Autumn.
- Significantly high concentrations of As Cananéia all the seasons, except for Autumn and high concentrations of Fe Winter, Autumn and Springtime.
- High concentrations of As and Fe was detected in oysters cultivate in Cananéia. These results have already been obtained in others sites of oysters cultivate. The high values of As some time is because of the background of the area. We suggest more studies to verify this cause.

### Seasonal Variations

Elements	Spring			Summer			Autumn			Winter		
	Cananéia	Bertioga	Santos	Cananéia	Bertioga	Santos	Cananéia	Bertioga	Santos	Cananéia	Bertioga	Santos
Hg	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low
Cr	Low	Low	Low	Low	Low	Low	Low	High	Low	Low	High	Low
Co	Low	Low	Low	High	Low	High	Low	Low	Low	Low	Low	High
Se	Low	Low	Low	High	Low	Low	Low	Low	Low	High	Low	High
Fe	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	High
Pb	Low	Low	Low	Low	High	Low	Low	Low	Low	Low	Low	Low
Zn	Low	Low	High	Low	Low	High	Low	High	Low	High	High	High
Cd	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low
As	High	Low	Low	High	Low	Low	Low	Low	Low	High	Low	Low

Low concentration  
High concentration

- The accumulation of these elements in the organisms is probably due to the presence of domestic sewage, since in Winter there is an increase in rainfall in Santos' Estuary, resulting in an increased transport of xenobiotics from the mainland into the estuary.

### Conclusions

The INAA and AAS methods allowed the determination of the concentrations of As, Cd, Co, Cr, Fe, Hg, Pb, Se and Zn with appropriate accuracy, as confirmed by analysis of the NIST SRM 1566b "Oyster Tissue". For the study of bioaccumulation of trace elements among the sites of oyster collection, it was verified that Canal de Santos presented the largest concentrations of elements studied in most cases. Regarding the seasonal variation, it can be observed that in winter there was a greater accumulation of the elements. In due to the human consumption a special warning should be given for the elements Cr, Se and specially Zn.