

**THE USE OF DIATOMITE ON WATER QUALITY ANALYSIS OF SANTOS AND SÃO VICENTE
ESTUARIES – SAO PAULO, BRAZIL**

Lilian Polakiewicz^{1,*}; Evelyn Loures de Godoi¹, Pérola de Castro Vasconcellos²; Nilce Ortiz¹,

Maria Aparecida Faustino Pires

Abstract

The quality of the brackish water was analyzed in two sampling spots with different environmental impact, the first spot was located near a commercial harbor with loading activities of chemical products – Santos and the second spot was located near a mangrove area, with biogenic contribution - Sao Vicente, the sampling procedures were conducted from March to July, 2006. The analysis of the water samples was performed measuring the physical and chemical parameters, and the ceramic sampler with diatomite spheres were deposited in the sampling spots during 30 days. The highest phosphorous values were observed for Santos and the total concentration of polycyclic aromatic hydrocarbon - PAH, adsorbed by diatomite were in the range of 294,61 to 764,70 ng g⁻¹ (mainly composed by fluorene and phenanthrene) in both spot sites. The adsorption process of lead and phosphate had been carried in laboratory to the determination of the adsorption properties and the adsorption kinetic model for the toxic compounds measured at sampling areas.

Resumo

A qualidade da água salobra foi analisada em dois locais com diferentes impactos ambientais, o primeiro característico de atividade antrópica portuária como a carga e descarga de produtos químicos – Santos e o segundo próximo a área mangue, com contribuição biogênica – São Vicente, entre os meses de março a julho de 2006. A análise da água foi realizada por

¹ Center of Environmental Chemistry - CQMA Institute for Energy and Nuclear Research - IPEN, Av. Lineu Prestes, 2242, Cidade Universitária, CEP 05508000, São Paulo / SP - Brazil. (* lpolakie@ipen.br)

² Chemical Institute – Universidade São Paulo, Av. Prof. Lineu Prestes, 748 - Cidade Universitária, CEP 05513970 - São Paulo - SP – Brazil

meio de medidas dos parâmetros físico-químicos e de um amostrador cerâmico com esferas de diatomito depositado nas áreas de coleta pelo período de 30 dias. Os maiores teores de fósforo foram obtidos em Santos e a concentração total de hidrocarboneto policíclico aromático - HPA, adsorvido pelo diatomito, variou de 294,61 a 764,70 ng g⁻¹ (predominantemente fluoreno e fenantreno) nos dois locais amostrados. Ensaio de adsorção de chumbo e fósforo foram realizados em laboratório para a determinação das propriedades adsorventes e o estabelecimento do modelo cinético de adsorção de compostos tóxicos encontrados na área de estudo.

1. Introduction

The estuaries of Santos and Sao Vicente are examples of the environmental degradation in Brazilian coastal area, located at Sao Paulo State. There is an important commercial harbor, and the largest industrial chemical complex of Brazil (CETESB, 2001). The harbor is responsible for 26.7% of total Brazilian commercial transport. The input and output of chemical and mineral goods have also contributed to the increase the local pollution. Since the 70's the Cubatão industrial complex, has been the most important petrochemical and metallurgical industrial complex with about 130 industries. The complex has been also responsible for more than 100 ton/month of toxic compounds discharge of zinc, phenol, mercury and oil (CETESB, 1986) in the estuary system. The environmental impact of Santos Estuary is also increased by the discharge of raw sewage water from Billing's reservoir which flows directly to the Cubatão River and from the river to the estuary. The sanitary discharge of Santos Harbor and domestic sewage discharge of the city were also responsible for environmental degradation of the estuaries (TOMMASI, 1979).

During 20 years were registered 153 ships transport accidents in the estuary system, with the spilling of 76% of inflammables from leaked tanks, (CETESB, 2006). The flow rate of the estuary water is considered low which reduces the water circulation and the possible

dilution of pollutants. The Santos estuary periodically is also suffering the dragger processes which has the main objective is guarantee the enough depth on canal for ships transportation. The dragger process represents sediment movement with the possibility of PAHs dissolution, mainly those PAHs with low molecular weight (TOLUN et al, 2006).

The Sao Vicente estuary, located near the mangrove area, has also been affected by urban occupation mainly due to precarious sanitary installations. The area represents an important shelter for species reproduction and has been suffering a continuous ecological degradation by anthropogenic activities. The determination of the hydrocarbon compounds in water is important to assess the source of anthropogenic contaminant.

Hydrocarbons are important compounds found in the environment as complex mixtures from multiple sources: biogenic, petrogenic and pyrogenic (MEDEIROS and BÍCEGO, 2004). The biogenic and anthropogenic inputs can be identify using their “signature” composed by specific organic compounds which maintain the information about their origins and their structural modifications that can be occurred during their transport.

The geochemical markers can be used as an indication of the hydrocarbon decomposition, the residence time, stability and transport mechanisms, accordingly with their physical-chemical properties (MEDEIROS and BÍCEGO, 2004). There are many hydrocarbons used as geochemical markers, the study emphasizes the polycyclic aromatic hydrocarbons (PAHs). PAHs are composed by benzene rings connected in different arrangements resulting in an important class of environmental contaminants with carcinogenic and mutagenic potential. There are several reports of the cancer in marine animals when the natural habitat is located in the vicinity of oil and PAHs ocean spills (BOONYATUMANOND et al, 2006). The PAHs are included in the United States Environmental Protection Agency - US EPA hazardous list and in the European Union priority lists of pollutants due to their environment concern (BOONYATUMANOND et al, 2006; MANOLI and SAMARA, 1999). PAHs are introduced

into the environment mainly via natural and anthropogenic combustion process (MANOLI and SAMARA, 1999). They have persistent nature and hydrophobic properties including high affinity for solids particles with the tendency to be accumulated in sediments of coastal areas. These properties can be important in adsorption studies natural adsorbents, as diatomite. The diatomite is chemically composed by natural amorphous silica originated as diatom frustules, obtained as fossils deposits called diatomaceous sedimentary rocks (KASTIS et al, 2006; YANG et al, 2003).

The project aims the development of a tool to assess the water quality and to use it in environmental monitoring and control. The ceramic sampler (CS) was placed on coastal waters for three to four weeks and after saturation the PAH compounds were desorbed and analyzed. The results indicated that the CS was suitable for the adsorption of these markers compounds of environmental pollution.

2. Materials and Methods

2.1 Estuaries water measurements - Physical and chemical monitoring

The ceramic sampler main composed by diatomite pellets was used to adsorb the toxic compound present in sampling area located at the estuaries of Santos and Sao Vicente shown in the **Figure 1**. The CS was deposited in the monitoring areas for four weeks. Then, physical and chemical water quality parameters were measured and the CS was conditioned.

The first sampling site (site 1) is located near Santos Commercial Harbor on the geographic coordinates of 23°59'30.06''S and 46°18'04.84''W. The second sampling site (site 2) is located near Sao Vicente city 23°58'52.49''S and 46°23'33.45''W. The two sampling sites were chosen considering the differences due environmental impact. The site 1, near the Santos harbor area, has remarkable anthropogenic influences and the site 2 located near a mangrove area is expected to show the biogenic influence. The water quality parameters were measured and the CS was changed monthly in both sites.

2.2 Adsorption process measurements - Phosphorous removal

The CS has been designing in laboratory experiments to obtain the better performance on adsorption process for water quality monitoring and control. This process has been performed based on the phosphorous removal, to study the diatomite adsorption process, kinetic and saturation. The phosphorous compound was chosen to be the most common toxic compound found on surface water located in urban areas with dense pollution, usually by sewage water discharge.

The adsorption process of the diatomite pellets used on CS preparation have been studied and adapted accordingly with the designed adsorption characteristics. The Phosphorous adsorption process were studied in batch using magnetic stirrer with 500 mL of brackish water (salinity of 29‰) and the concentration were determined on different aliquots collected on 0, 10, 30, 120, 200, 240, 260, 300 and 360 minutes. The final phosphorous concentration was measured in the aliquot of 306min. The initial and the final concentrations were varying accordingly with the adsorption properties and the temperature was kept constant during all adsorption process.

The phosphorous concentrations on different aliquots were measured using the molybdenum complex formation, equipment for UV-VIS spectrophotometer Varian Carry-1E and the comparison with calibration curve prepared from phosphorous standardized solutions.

3. Results and Discussion

3.1 Physical and chemical monitoring results

The pH values measured were about 7 for both sampling sites. The water temperatures in Santos at summer season were usually higher of those measured on Sao Vicente, in winter the water temperature was lower in the range of 19.6°C and 20.1°C for both sites. The highest

values obtained for DO were measured in winter with 7.2 mg.L⁻¹ for Santos and 6.2 mg.L⁻¹ for Sao Vicente, in summer season the lower values were measured with 4.75 mg.L⁻¹ and 5.66 mg.L⁻¹ for Santos and Sao Vicente respectively. The obtained values can be observed at

Table 1.

The phosphorous content on both sites were higher in the summer than in the winter, on Santos the values ranging from 0.13 mg.L⁻¹ to 0.37 mg.L⁻¹ and in the winter the values varied from 0.09 mg.L⁻¹ to 0.04 mg.L⁻¹. The values measured at Sao Vicente were usually lower than Santos, varying from 0.05 mg.L⁻¹ to 0.11 mg.L⁻¹. The salinity of Santos was always higher than Sao Vicente, with the values in the range of 31‰ to 35‰ and 25‰ to 31‰ respectively.

Table 1: Physical and chemical parameters of water analysis at Santos and Sao Vicente estuaries.

<i>Date (2006)</i>	<i>Local</i>	<i>Enviroment Temperature (°C)</i>	<i>Water Temperature (°C)</i>	<i>pH</i>	<i>Dissolved Oxygen (mg.L⁻¹)</i>	<i>Phosphorous Content (mg.L⁻¹)</i>	<i>Salinity (‰)</i>
03/02	Santos	20.2	30.0	7	4.75	0.37	35
04/18	Santos	25.0	24.0	7	4.60	0.13	---
	São Vicente	25.0	23.5	7	5.66	0.11	25
05/23	Santos	17.0	21.9	7	7.20	0.09	34
	São Vicente	17.0	20.1	7	6.20	0.09	30
06/28	Santos	17.0	19.9	7	4.54	0.08	34
	São Vicente	18.0	20.1	6	5.80	0.06	33
08/02	Santos	17.0	19.9	7	5.00	0.06	31
	São Vicente	17.0	19.6	7	5.80	0.05	27
09/05	Santos	15.0	20.2	7	---	0.04	35
	São Vicente	15.0	19.9	6		0.05	27

The high values of DO and phosphorous content measured at summer season on both

sampling sites can be considered an indication of the environmental impact due the discharge of domestic sewage water, which higher accordingly with the increasing number of inhabitants for tourism activity at summer season.

The Brazilian Environmental Resolution (CONAMA 357) establishes values for water quality parameters to classify the continental water accordingly with their possible use. The saline water class 1 represents the water adequate for recreation activities of first contact and protection of aquatic communities and the class 2 is the water which can be use only for second contact activities, including fishing.

The sampling site 1 - Santos is considered saline water according with the Resolution, with salinity values over that 30‰, in this site the DO values indicate the estuary as class 2 and 3 (the classes 3 are destined just for navigation) unsuitable for swimming activities. There is no indication about the limit of phosphorous content for class 3 in this resolution. The site 2 - Sao Vicente, show influence from mangrove area reducing their salinity, the water are considered brackish and class 1 and 2, the DO values obtained at São Vicente site indicate class 1.

3.2 Estuaries water - PAH monitoring results

The adsorbed PAHs concentrations are descript at **Table 2**. The total PAHs concentrations were ranged from 190.03 ng.g⁻¹ to 565.80 ng.g⁻¹. The highest PAHs values were found at Santos site (167.34 ng.g⁻¹) for fluorene, 149.97 ng.g⁻¹for acenaphthene and 146.84 ng.g⁻¹for phenanthrene. These compounds were also measured at Sao Vicente at lower concentrations; the values measured were 49.99 ng.g⁻¹, 43.56 ng.g⁻¹ and 46.48 ng.g⁻¹, respectively.

Naphthalene was found at lower concentration at both monitoring sites (25.93 ng.g⁻¹

at Santos and 8.32 ng.g^{-1} at Sao Vicente). The Anthracene was found at Santos and Sao Vicente sampling sites in the concentration of 43.33 ng.g^{-1} and 13.82 ng.g^{-1} respectively. Benzo(a)anthracene concentration was lower at São Vicente site (0.77 ng.g^{-1}) than at Santos site (2.54 ng.g^{-1}). The Benzo(a)pyrene, considered a mutagenic compound was measured only at Santos (22.35 ng.g^{-1}). The PAHs compounds fluoranthene and Benzo(k)fluoranthene were found at both sites in low concentrations.

The origin index indicates presence of a certain compound is related with anthropogenic activity developed in the area of influence. The petrogenic contamination was characterized by the predominance of PAHs with low molecular weight-LMW (tri- and four rings) (NEFF, 1979; WISE et al., 1988; BERNER et al., 1990; TOLUN et al, 2006) and PAHs with higher molecular weight-HMW predominant on pyrolytic contamination (MUEL and SAGUEM, 1985; TOLUN et al, 2006). Based on PAHs identification observed on both study sites, the higher concentrations of PAHs were of lower molecular weight indicating the influence of petrogenic contaminants in Santos, and the analyzed compounds are an indication of petrogenic activity and pyrolytic contribution (**Figures 2 and 3**). The dragger of the Santos channel can be a possibility for the LMW increasing due its dissolution from the channel sediment, this effect have the tendency to enhance the LMW content adsorbed at CS during the monitoring time.

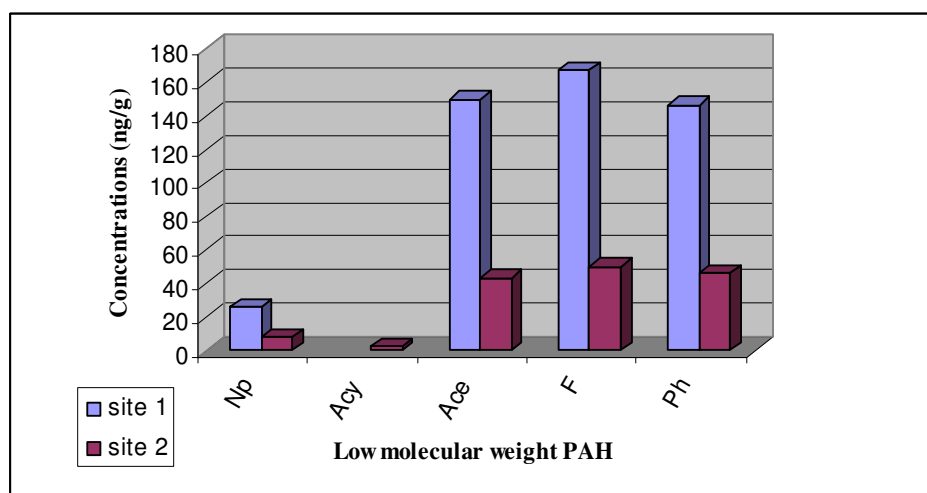
The results observed at **Figures 2 and 3** shows a predominance of LMW compounds on both sampling sites and even when the HMW compounds found are in very low concentrations, except for anthracene compound.

Table 2: The concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) on ng/g, measured at CS after saturation.

PAHs (ng/g)	Santos - site 1	São Vicente - site2
Naphthalene - Np	25.93	8.32
Acenaphthylene - Acy	---	2.25
Acenaphthene - Ace	149.97	43.56
Fluorene - F	167.34	49.99
Phenanthrene - Ph	146.84	46.48
Anthracene - An	43.33	13.82
Fluoranthene - Fl	0.42	0.03
Pyrene - Py	0.76	0.72
Benzo(a)anthracene - B(a)An	2.54	0.77
Chrysene - Chry	0.89	21.66
Benzo(b)fluoranthene - B(b)Fl	0.11	0.15
Benzo(k)fluoranthene - B(k)Fl	0.50	0.02
Benzo(a)pyrene - B(a)Py	22.35	---
Indeno(1.2.3-cd)pyrene - I(1,2,3-cd)Py	4.8	1.83
Benzo(g,h,i)perylene - B(g,,h,i)Pe	---	0.41
TOTAL	565.80	190.03

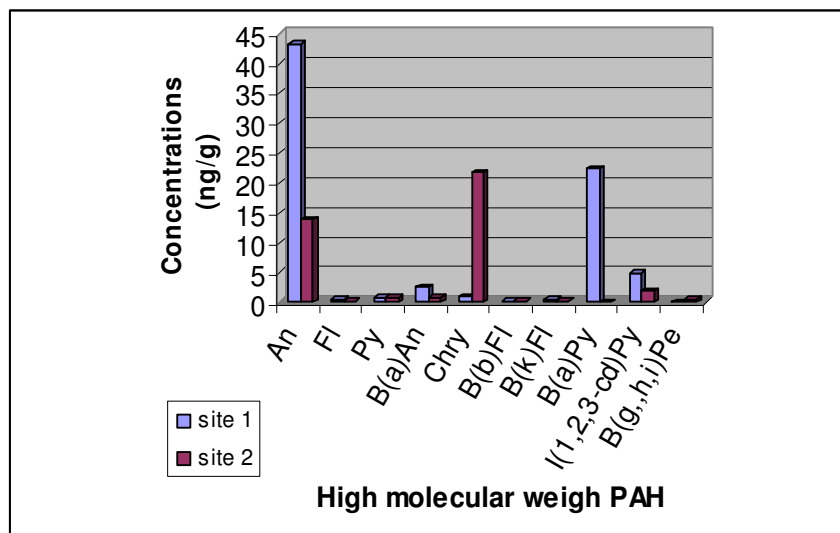
Where: Np = Naphtelene, Acy = Acenaphthylene, Ace =Acenaphthene, F =

Fluorene and Ph = Phenanthrene



Where: Np = Naphtelene, Acy = Acenaphthylene, Ace = Acenaphthene, F = Fluorene and Ph = Phenanthrene

Figure 2: The concentrations of PHAs compounds with low molecular weight at two sample sites (ng/g). Site 1: Santos and Site2: São Vicente.



Abreviation: An - Anthracene, Fl - Fluoranthene, Py - Pyrene, B(a)An - Benzo(a)anthracene, Chry - Chrysene, B(b)Fl - Benzo(b)fluoranthene, B(k)Fl - Benzo(k)fluoranthene, B(a)Py - Benzo(a)pyrene, I(1,2,3-cd)Py - Indeno(1.2.3-cd)pyrene, B(g,,h,i)Pe - Benzo(g,h,i)perylene

Figure 3: Concentrations of compounds with high molecular weight – HMW at two sample sites (ng/g). Site 1: Santos, site2: São Vicente.

3.3 CS - Adsorption process measurements

The total removal percentage, the initial and final concentrations for phosphorous adsorption processes can be observed at **Table 3**. The removal percentage obtained for pH 5 was in the range of 13.03 % to 57.97% and for pH 7 were in the range of 6.90% to 12.96%. The diatomite pellets showed low removal percentages in comparison with commercial adsorbents. The low adsorption velocity is adequate and also necessarily to perform water quality monitoring and control, the CS saturation has to design to happen after three or four weeks, the monitoring and deposition time in the estuary or in controlled continental surface water.

Table 3: Total phosphorous removal percentage for CS pellets.

<i>pH</i>	<i>Concentração Inicial (mg.L⁻¹)</i>	<i>Concentração Final (mg.L⁻¹)</i>	<i>Percentual de Remoção (%)</i>
5	0.46	0.40	13.03
	1.26	0.98	21.96
	0.73	0.31	57.97
	1.39	1.14	17.78
	0.90	0.77	14.31
7	0.47	0.44	6.90
	1.39	1.30	7.00
	0.81	0.73	9.76
	1.45	1.34	7.04
	0.85	0.74	12.96

4. Conclusion

The phosphorous content measured at Santos estuary in summer season were always higher than in winter, this effect is an indication of the increasing of pollutants with domestic sewage water discharge affected by the increasing number of inhabitants for tourism activity at summer season. The ceramic sampler shows adsorption properties adequate to be used as a tool for water quality monitoring and control, mainly for organic compound after sedimentation. The use of CS allow the determination and quantification of the PAH compounds suspended in water on both sampling sites, to study an indication of the pollution of anthropogenic activities with higher influence at site 1 – Santos (with higher concentrations). The Santos Harbor and the harbor for Cubatão industrial complex may be the most important source of those compounds with the anthropogenic activities as the combustion of fossil fuels, waste incineration, coke and asphalt production, oil refining and other industrial activities characteristics sources of the compounds. The PAH concentration measured at sampling site 2 -São Vicente were lower than site 1, this effect was expected considering the location of site 2 near mangrove area and distant from the commercial. The benzo(a)anthracene and benzo(a)pyrene compounds are considered carcinogenic to humans

according with International Agency for Research on Cancer (IARC) and United States Environmental Protection Agency (US EPA).

5. Acknowledgements

The authors acknowledge The State of Sao Paulo Research Foundation - Fapesp and The National Council for Scientific and Technological Development - CNPq for the financial support.

6. References

- BERNER Jr B.A., BRYNER N.P., WISE S.A., MULHOLLAND G.H., LAO R.C., FINGAS M.F. Polycyclic aromatic hydrocarbon emissions from combustion of crude oil on water. *Environ Sci Technol.* 24:1418–27, 1990.
- BOONYATUMANOND, R., WATTAYAKORN, G., TOGO, A. and TAKADA, H. Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Marine Pollution Bulletin*. Article in Press, 2006.
- CETESB (Companhia de Tecnologia de Saneamento Ambiental) *Avaliação da toxicidade das águas e sedimentos dos rios e efluentes industriais da região de Cubatão 2*. São Paulo, 42 pp, 1986.
- CETESB (Companhia de Tecnologia de Saneamento Ambiental) site oficial <http://www.cetesb.sp.gov.br>, em março de 2006.
- CETESB (Companhia de Tecnologia de Saneamento Ambiental). *Sistema Estuarino de Santos e São Vicente*. Secretaria do Meio Ambiente, São Paulo, 178 pp, 2001.
- KASTIS, D., KAKALI, G., TSIVILIS, S., STAMATAKIS, M.G. Properties and hydration of blended cements with calcareous diatomite. *Cement and Concrete Research*. Article

in Press, 2006

- MANOLI, E., SAMARA, C. Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *Trends in Analytical Chemistry*, vol. 18, no. 6, pp.417-428, 1999
- MEDEIROS, P.M., BÍCEGO, M.C. Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. I. Santos, SP-Brazil. *Marine Pollution Bulletin*. v. 49, Issue 9-10, p. 761-769, 2004.
- MEDEIROS, P.M., BÍCEGO, M.C. Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. II. São Sebastião, SP-Brazil. *Marine Pollution Bulletin*. v. 49, p. 892-899, 2004.
- MUEL B., SAGUEM S. Determination of 23 polycyclic aromatic hydrocarbons in atmospheric particulate matter and of Paris area and photolysis by sunlight. *Environ Sci Technol*. 19:111–31, 1985.
- NEFF J.M. Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates and biological effects. *London, UK: Applied Science Publishers*. p. 262, 1979.
- TOLUN, L., MARTENS, D., OKAY, O.S., SCHRAMM, K.W. Polycyclic aromatic hydrocarbon contamination in coastal sediments of the Izmit Bay (Marmara Sea): Case studies before and after the Izmit Earthquake. *Environment International* v.32 pp 758–765, 2006.
- TOMMASI, L.R. Considerações ecológicas sobre o sistema estuarino de Santos (SP). Tese de Livre docência. Universidade de São Paulo. Universidade de São Paulo. vol. 2, 1979.
- WISE, S.A., BENNER, B.A., BYRD, G.D., CHESLER. S.N., REBBERT, R.E., SCHANTZ, M.M. Determination of polycyclic aromatic hydrocarbons in a coal tar standard reference material. *Anal Chem*. 60:887–94, 1988.
- YANG, Y., ZHANG, J., YANG, W., WU, J., CHEN, R. Adsorption properties for urokinase

on local diatomite surface. *Applied Surface Science*, v. 206, Issue 1-4, p. 20-28, 2003.