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Influence of a Brazilian sewage outfall on the toxicity and contamination of adjacent sediments

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Abstract

The submarine sewage outfall of Santos (SSOS) is situated in the Santos Bay (São Paulo, Brazil) and is potentially a significant source of contaminants to the adjacent marine ecosystem. The present study aimed to assess the influence of SSOS on the sediment toxicity and contamination at Santos Bay. At the disposal site, sediments tended to be finer, organically richer and exhibited higher levels of surfactants and metals, sometimes exceeding the "Threshold Effect Level" values. The SSOS influence was more evident toward the East, where the sediments exhibited higher levels of TOC, total S and metals during the summer 2000 sampling campaign. Sediment toxicity to amphipods was consistently detected in four of the five stations studied. Amphipod survival tended to correlate negatively to Hg, total N and % mud. This work provides evidence that the SSOS discharge affects the quality of sediments from Santos Bay, and that control procedures are warranted.

Keywords: Sewage; Sediments; Toxicity, Marine pollution; Santos; Sewage outfall

1. Introduction

Urban sewage is considered the main cause of marine and estuarine pollution in Brazil (Tommasi, 1987a). Most Brazilian coastal cities do not have proper facilities to collect, treat and dispose of sewage. In Baixada Santista, situated at the central shore of the State of São Paulo, a sanitation program was conducted between late 1970s and early 1990s, and involved the construction of collection systems in some cities and the installation of four submarine sewage outfalls along the shore. The oldest of them is the submarine sewage outfall of Santos (SSOS), which has been operating since 1978 (Occhipinti, 1972) and serves the cities of Santos and São Vicente. According to Rachid (2002) the system was designed to accommodate a maximum population of 1.322 million people. Nowadays, this system receives contributions from approximately 99% of Santos and 40% of São Vicente residences.

The SSOS is considered a significant source of contamination to the Santos Bay, as it discharges untreated sewage into the sea (Rachid, 2002; Moser, 2002). This oceanic disposal system is comprised of a preconditioning plant and its respective sewage outfall. The pre-conditioning consists of a process in which the effluent is chlorinated, double screened (10 and 4 cm length), and sieved (1.5 mm rotation sieve), before being carried into the pipeline. There is not any further treatment (primary or secondary), as the sewage is essentially discharged untreated.

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The pipeline is built of concrete-covered steel (1.75 m internal diameter). It is 5 km long and discharges into the middle of Santos Bay 4 km from the beach at a depth of 12 m (Rachid et al., 1998). In the last 200 m of the pipeline, there are 40 diffusers, which function to increase the initial dilution of the effluent (Agudo, 1983; Hidroconsult, 1977). The maximum projected capability for the effluent flow is 7 $m^3 s^{-1}$, but the mean flow ranges between 0.6 and 1.6 $m^3 s^{-1}$.

The discharge of sewage into the sea in shallow waters should involve monitoring programs which assess the environmental impacts of its operation, periodic evaluations of the efficiency of the system, and implementation of improvements when possible. Throughout its history, the environmental effects produced by the SSOS discharges have not been adequately studied. Investigations regarding the effects are few and far between and do not consider the complexity of the possible effects and, therefore, are inconclusive (Rachid, 2002). In a preliminary study, toxicity was detected in sediments collected close to the outfall diffusers of SSOS, and the need of a detailed investigation in that area was warranted (Abessa et al., 1998). The objective of the present study was to evaluate the distribution of contaminants and toxicity of sediments collected in the vicinity of the Santos sewage outfall.

2. Materials and methods

Sediment samples were collected at five stations situated close to the sewage outfall diffusers (Fig. 1), using a 0.026 m^2 stainless steel Petersen grab sampler. Station locations were selected to assess spatial and temporal variations in sediment toxicity, as previously proposed by Abessa et al. (2001). Sampling campaigns were conducted in summer and winter 1998; summer and winter 1999; and summer 2000.

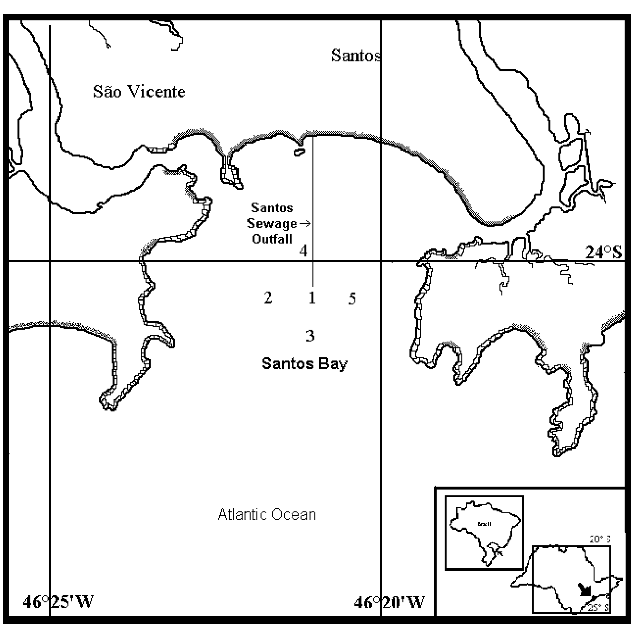

Fig. 1. Map showing the sampling stations close to the Santos Sewage Outfall diffusers.

From the retained material, only the 2-cm surficial layer from the sediment not in contact with the grab sampler walls was composited. Aliquots of the homogenized composite were then sub sampled for chemical, granulometric and ecotoxicological analyses. Control samples were collected at Ilhabela, in front of Engenho D'água Beach, located in the São Sebastião Channel (23.7701 °S–45.3592 °W). This choice was supported by the fact that in Baixada Santista the sediments are influenced by anthropogenic activities to varying degrees, thus using reference sediments from that region is not advisable (Abessa, 2002).

The carbonate contents were estimated, according the method described by Gross (1971). Sediments were weighed, (30 g), digested in 10% nitric acid for 2 days, washed with distilled water and dried at 60 °C for 24 h and then weighed again. Weight differences corresponded to the carbonate contents in each sample.

Grain size distribution was analyzed by the dry sieving method (Suguio, 1973). Sediment (30 g) aliquots were dried at 60 °C for 48 h. They were then sieved for 15 min, using a set of sieves with 0.5∅ intervals in the Went-Worth scale. Fractions retained in each sieve were weighed, allowing estimates of sand and mud content and the granulometric classification of the samples (Shepard, 1954; Folk and Ward, 1957).

The contents of total organic carbon (TOC), nitrogen and sulfur were measured using a LECO CNS 2000 automated analyzer, which uses the Micro Kjeldahl method (McKenzie and Wallace, 1954). According to the protocol, 100 mg of sediment were separated, and maintained for 48 h in 10% HCl to eliminate the carbonates. Then, the samples were washed with distilled water and lyophilized, and 0.5 g aliquots were separated and introduced into the analyzer.

The concentration of the following metals was analyzed: Al, Fe, Cd, Cr, Co, Hg, Ni, Pb and Zn. Before the extraction, the sediment samples were dried at ambient temperature and sieved in a 1 mm net. For Al, Cr and Fe, total digestion in high pressure microwaves system was used (CEM Corporation, model MDS—2000). The acid extraction solution consisted of a mixture containing Milli-Q water, HNO_3, HF, and HCl, according to recommendations of Krause et al. (1995). For Cd, Co, Pb and Zn, Aqua Regia and $HClO_4$ were employed in the extraction. Analyses were made using a fast sequential Atomic Absorption Spectroscope. For Hg, extractions were made in volumetric flasks heated for 30 min at 90 °C (Akagi and Nishimura, 1991), using Aqua regia and $HClO_4$. The extracted solutions were then introduced into a system of Flux Injection for Cold Vapour generation (FIA-CV-AAS) (Fostier et al., 1995), and analyzed with an Atomic Absorption Spectroscope (VARIAN, AAS 220-FS) at a wavelength of 253.7 nm. As Quality Assurance and Quality Control procedure (QA/QC), the methods were verified using certificate reference sediment (Buffalo River Sediment®).

The results obtained for the chemical analysis of metals were compared to the Canadian Sediment Quality Guidelines, which proposes two assessment values (Smith et al., 1996). The threshold effect level (TEL) is referred as the concentration below which adverse effects are expected to accur rarely. The probable effect level (PEL) represents the level above which adverse effects are expected to occur frequently.

Surfactants concentrations in sediments were estimated by the methylene blue active substance (MBAS) method (APHA/AWWA/WEF, 1998) after extraction by elutriation in distilled water (Abessa, 2002). This method consists of transferring methylene blue, a cationic dye, from an aqueous solution into an organic liquid, through the ion pair formation by MBAS anion and the methylene blue cation. The intensity of the resulting blue color in the organic phase is a measure of MBAS. The procedure is simple and comprises three successive extractions from acid aqueous medium containing methylene blue into chloroform, followed by an aqueous backwash and measurement of the blue color in the chloroform by spectrophotometry at 652 nm.

Sediment samples from 1998 were not analyzed for metals and surfactants.

Whole sediment toxicity tests were conducted using the amphipod *Tiburonella viscana,* according to the procedure described by Melo and Abessa (2002). One day before the start of the test, each sediment sample was thoroughly homogenized within its storage container by stirring, and aliquots were distributed into the test chambers (1-l polyethylene beakers). Sediments were not sieved. The test chambers were filled to 2 cm depth with the test sediments and filtered seawater up to 750 ml and then maintained overnight at 25 ± 2 °C with gentle aeration. On the next day, 10 amphipods were added to each test chamber and the tests commenced. Amphipods that did not bury within 1 h were removed and replaced. Three to five replicates per test sediment were prepared, respectively. The tests were conducted at 25 ± 2 °C, under constant aeration and lighting. After ten days, the contents of the test-chambers were gently sieved through a 0.5-mm screen and the surviving amphipods were counted. Missing organisms were considered dead. The mortalities were compared by the one-way analysis of variance (ANOVA), followed by Dunnett's *t*-test (Zar, 1984). The dissolved oxygen concentration, salinity and pH of the overlying water in the test chambers were measured at the beginning and termination of the tests. The water temperature was monitored daily.

Correlations between toxicity, chemical contamination and sediment properties were tested using multiple correlation analysis.

3. Results

3.1. Summer 1998

Results from the whole sediment toxicity test showed significant mortalities in organisms exposed to sediment from stations 1, 3 and 4 (Table 1). Amphipod survival correlated negatively with % mud, total N concentrations and carbonate contents.

Tested sediments were classified as sandy muds (stations 1 and 5), muddy sand (station 3) and sands (stations 2, 4 and control). Fines were found at stations situated close to sewage diffusers and also at the southern and eastern stations. Carbonate contents tended to be higher at these stations. Sediments from stations 2 and 5 had higher TOC contents, followed by station 3. For total N and S concentrations, the greatest values were observed at stations 1, 3 and 5. These results are presented in Table 2.

3.2. Winter 1998

During the winter 1998, stations 2, 4 and the control were predominantly sandy, whereas in at stations 1, 3 and 5 the sediments were a mixture of sand and mud (Table 3). Carbonate contents were higher in sediments from stations 3 and 5, reaching 16.81% and 27.89%, respectively. The results observed for TOC were similar to that obtained in the summer, with higher contents in sediments from stations 2, 5 and 1. Concentration of total S was high only in sediment from station 1, whereas the greatest N concentrations were measured in sediments from stations 1, 3 and 5. In this campaign, sediment toxicity was observed in stations 1, 3, 4 and 5 (Table 1). Amphipod survival correlated negatively with the contents of mud and total N.

3.3. Summer 1999

During the summer 1999, the sediments from stations 1 and 5 were composed of sandy mud whereas stations 2, 4 and the control were sandy (Table 4). Sediment from station 3 was classified as muddy sand. Contents of $CaCO_3$ were higher in sediments from stations 3 and 5. The higher TOC contents were observed in sediments from stations 1 and 5. Concentrations of total S and N were higher in sediments of station 1, with moderate values in stations 3 and 5 and low levels in sediments from stations 2 and 4.

Results of chemical analyses are presented in Table 5. Concentrations of Al and Fe were similar in sediments

Table 1
Mean survival rates of amphipods exposed to sediments collected near the Submarine Sewage Outfall of Santos

Station	1998		1999		2000
	Summer	Winter	Summer	Winter	Summer
1	65.0 ± 13.2*	64.0 ± 4.2*	68.75 ± 12.5*	87.5 ± 13.2	83.8 ± 12.5
2	76.7 ± 15.3	79.0 ± 11.9	73.75 ± 16.5	87.5 ± 15.5	88.0 ± 9.1
3	58.3 ± 7.6*	65.0 ± 7.9*	68.75 ± 14.9*	95.0 ± 10.0	76.0 ± 9.6*
4	66.7 ± 5.8*	68.0 ± 16.8*	76.25 ± 14.9	75.0 ± 14.7	73.0 ± 11.0*
5	70.0 ± 5.0	70.0 ± 7.9*	68.75 ± 8.5*	75.0 ± 16.8	80.0 ± 19.6
Control	86.7 ± 2.9	96.0 ± 4.2	88.75 ± 10.3	93.8 ± 9.5	98.0 ± 4.5

*Significant different to the control ($p \leqslant 0.05$).

Table 2
Granulometric and organic enrichment characteristics of the tested sediments during the summer 1998

Station	% Sand	% Mud	% $CaCO_3$	TOC (%)	S (%)	N (%)
1	35.51	64.49	10.21	1.69	1.77	0.11
2	90.17	9.83	6.23	2.53	0.04	<0.01
3	50.53	49.47	23.07	0.61	0.60	0.08
4	95.02	4.98	5.4	0.09	0.02	0.01
5	36.66	63.34	20.67	1.27	0.59	0.12
Control	97.31	2.69	4.55	0.99	0.35	0.02

Table 3
Granulometric and organic enrichment characteristics of the tested sediments during the winter 1998

Station	% Sand	% Mud	% $CaCO_3$	TOC (%)	S (%)	N (%)
1	42.21	57.79	7.25	1.03	0.89	0.08
2	92.35	7.65	8.07	1.89	0.02	0.01
3	57.83	42.17	16.81	0.47	0.04	0.08
4	96.79	3.21	3.99	0.16	0.02	<0.01
5	41.65	58.35	27.89	1.87	0.48	0.11
Control	93.26	6.74	6.91	0.65	0.21	0.01

Table 4
Granulometric and organic enrichment characteristics of the tested sediments during the summer 1999

Station	% Sand	% Mud	% $CaCO_3$	TOC (%)	S (%)	N (%)
1	33.26	66.74	5.70	2.91	1.98	0.19
2	92.03	7.97	5.55	1.03	0.03	0.02
3	63.49	36.51	17.65	0.98	0.78	0.08
4	93.13	6.87	6.71	0.05	0.01	<0.01
5	39.75	60.25	13.32	1.98	0.69	0.10
Control	93.31	6.79	8.84	0.72	0.21	<0.01

of all tested stations. The levels were lower that those observed in the control. Cadmium and zinc concentrations were low in all the tested sediments. Levels of Pb were lower than TEL (Smith et al., 1996) but greater than the concentrations observed in the control sediment. The highest Pb concentration was observed in sediment from station 1 (17.34 $\mu g\ g^{-1}$). The concentrations of Cr were below the TEL, but in stations 1, 2 and 4 the levels were greater than was measured in the control sediment. Mercury was found in levels greater than the control in all tested sediments, and in sediment from station 1 the value was equal to the TEL (0.13 $\mu g\ g^{-1}$). Nickel levels were similar among samples, with the exception of station 1, where the concentration was above the TEL. Concentrations of Co were higher in sediments from station 1 and the control. The control sediment exhibited the highest MBAS concentration followed by the sediment from the station 1. Contents of Ni, Pb and Hg showed a positive correlation with % mud, whereas Ni and Hg concentrations correlated positively to TOC contents.

The toxicity test showed significant responses in animals exposed to sediments from stations 1, 3 and 5 (Table 1). *Tiburonella viscana* survival correlated positively with Al, Fe and Zn concentrations, and negatively with the contents of Ni, Pb, Hg, mud, TOC, S and N.

3.4. Winter 1999

In the winter 1999, sediments from stations 2, 4 and the control were predominantly sandy, whereas stations 1 and 5 were sandy mud. Sediment from station 3 was classified as muddy sand. The contents of carbonates

Table 5
Concentrations of metals and MBAS in sediments collected close to the Santos sewage outfall during the Summer 1999

Contaminant station	Al %	Fe %	Zn ($\mu g\ g^{-1}$)	Ni ($\mu g\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Cd ($\mu g\ g^{-1}$)	Cr ($\mu g\ g^{-1}$)	Co ($\mu g\ g^{-1}$)	Hg ($\mu g\ g^{-1}$)	MBAS ($\mu g\ g^{-1}$)
1	4.15	2.46	57.24	17.39	17.34	<0.50	34.77	8.55	0.13	9.77
2	4.43	1.96	52.79	14.43	13.68	<0.50	34.46	7.21	0.12	5.373
3	3.87	1.89	42.65	13.44	10.17	<0.50	23.46	6.92	0.08	6.84
4	4.33	2.14	50.71	15.16	15.36	<0.50	28.34	7.10	0.07	3.42
5	4.35	2.31	51.40	14.32	14.93	<0.50	23.95	7.39	0.10	6.84
Control	6.57	3.52	70.78	12.42	3.62	<0.50	24.83	8.57	0.03	10.25

were greater in sediments from stations 5, 3 and 2, respectively (Table 6). Levels of TOC were higher in sediments from stations 5, control, 1 and 2. Concentrations of total S tended to be low, and the higher values were observed in sediments from stations 1 and 5. Total nitrogen concentrations were high only in sediments from stations 3 and 5.

In the winter 1999, Al and Fe concentrations were higher in the control sediment (Table 7). Among the tested samples, sediment from station 1 presented the highest levels of these elements. Sediment from station 1 presented TEL exceedance for Cd, whereas in the resting samples the concentrations were considered low. Levels of Pb were similar among the samples, but station 1 sediment had a higher concentration (28.0 $\mu g\ g^{-1}$). Sediment from stations 1 and 2 exhibited levels of Cr above the TEL, whereas in the resting samples the concentrations were low. TEL exceedances were observed for Hg in sediments from stations 1, 4 and 5; and for Ni in stations 1, 3, 5 and the control. The results for Co and Zn were similar to those obtained in the summer 1999 campaign, with higher levels in stations 1 and the control. The highest MBAS estimated concentrations occurred in sediments from station 1.

In summary, sediment from station 1 presented the higher contents of metals, MBAS, TOC, total N and total S. In this study, concentrations of Ni, Pb, Cd and Hg correlated positively to mud content. This result appears to indicate that these elements tend to accumulate in areas where sediments are finer. With regards to TOC, this variable was positively correlated to Al, Fe and Co concentrations.

In the toxicity test conducted in the winter 1999, no sample produced a significant response for *T. viscana* (Table 1). A positive correlation was observed between *T. viscana* survival and sediment Zn concentration.

3.5. Summer 2000

Sediments from stations 1, 2, 4 and the control were composed primarily of sand, whereas for stations 3 and 5, the sediments were sandy muds. The carbonate content was greater in sediment from station 3. The content of TOC was higher in the control sediment, but in the samples from Santos the highest levels were measured in sediments of stations 2 and 5, respectively. The highest S concentration was observed at station 1. Samples from stations 1 and 5 showed the highest total N contents (Table 8).

As observed in the other campaigns, the control sediment had the highest Al and Fe concentrations. Among samples from Santos, highest concentrations were observed in sediment from station 5. Concentrations of Cd, Pb and Cr were below the TEL in all analyzed samples; however sediment from station 5 showed the higher level of these elements. This sediment also had the highest concentration of Co. The highest Hg concentrations were observed in the sediments from stations 4 and 5, exceeding the TEL. Exceedance of TEL were also observed for Ni, in the sediment from station 5 and in the control. These two samples also exhibited the greatest Zn concentrations. The highest MBAS contents were observed in the sediments from stations 1 and 2 (Table 9). The mud content correlated with the concentrations

Table 6
Granulometric and organic enrichment characteristics of the tested sediments during the winter 1999

Station	% Sand	% Mud	% $CaCO_3$	TOC (%)	S (%)	N (%)
1	32.4	67.6	2.13	1.62	0.51	0.07
2	91.11	8.89	10.96	1.23	0.02	<0.01
3	53.21	46.79	11.67	0.61	0.03	0.18
4	94.49	5.51	5.81	0.21	0.01	0.01
5	29.71	70.23	16.92	1.98	0.59	0.21
Control	97.89	2.11	5.43	1.72	0.41	<0.01

Table 8
Granulometric and organic enrichment characteristics of the tested sediments during the summer 2000

Station	% Sand	% Mud	% $CaCO_3$	TOC (%)	S (%)	N (%)
1	72.23	27.67	8.12	1.01	1.12	0.09
2	91.12	8.88	10.23	1.73	0.07	0.01
3	64.31	35.69	16.31	0.91	0.79	0.06
4	96.09	3.91	7.88	0.96	0.04	<0.01
5	32.41	67.39	12.32	1.53	0.45	0.09
Control	95.31	3.69	8.9	1.87	0.22	0.04

Table 7
Concentrations of metals and MBAS in sediments collected close to the Santos sewage outfall during the winter 1999

Contaminant station	Al %	Fe %	Zn ($\mu g\ g^{-1}$)	Ni ($\mu g\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Cd ($\mu g\ g^{-1}$)	Cr ($\mu g\ g^{-1}$)	Co ($\mu g\ g^{-1}$)	Hg ($\mu g\ g^{-1}$)	MBAS ($\mu g\ g^{-1}$)
1	6.06	2.47	83.26	26.50	28.00	0.85	74.92	13.50	0.11	22.96
2	4.90	1.96	53.13	14.63	14.00	<0.50	111.72	7.23	0.08	4.40
3	4.15	1.91	57.55	16.68	17.00	<0.50	37.23	6.78	0.10	2.93
4	4.55	2.14	51.29	15.10	15.50	<0.50	31.37	7.28	0.18	4.40
5	4.67	2.31	52.32	16.13	14.50	<0.50	21.41	7.40	0.18	4.40
Control	6.38	2.77	75.30	16.48	4.96	<0.50	34.05	11.50	0.04	4.40

Table 9
Concentrations of metals and MBAS in sediments collected close to the Santos sewage outfall during the summer 2000

Contaminant station	Al %	Fe %	Zn (μg g^{-1})	Ni (μg g^{-1})	Pb (μg g^{-1})	Cd (μg g^{-1})	Cr (μg g^{-1})	Co (μg g^{-1})	Hg (μg g^{-1})	MBAS (μg g^{-1})
1	3.99	1.78	50.63	12.51	12.31	<0.50	14.34	5.80	0.09	7.33
2	3.94	1.78	42.84	11.40	11.34	<0.50	5.46	5.15	0.09	6.35
3	4.31	2.02	44.59	12.39	8.92	<0.50	17.97	5.40	0.05	4.84
4	4.19	2.18	51.51	14.43	16.29	<0.50	16.99	5.61	0.05	4.40
5	5.25	3.25	65.59	20.91	25.95	0.65	38.01	11.15	0.17	4.89
Control	7.14	3.20	78.97	17.37	14.74	0.50	22.03	12.86	0.03	5.37

of Cd, total S, Cr, total N and $CaCO_3$, whereas the TOC percent correlated with Al, Fe, Zn and Co concentrations.

In the campaign conducted in the summer 2000, the organisms exposed to sediments from stations 3 and 4 exhibited significant mortality (Table 1). A negative correlation was observed between amphipod survival and Hg and total ammonia in porewater, whereas positive correlations were observed for Al, Zn, Co and TOC levels.

4. Temporal variations and trends

The particle size distribution was relatively consistent over time for a particular station. Stations 2 and 4 exhibited sandy sediments, followed by station 3. For stations 1 and 5, the sediments had a higher percent of mud. The results showed that the granulometric distribution around the diffusers can vary spatially, however, in each station the temporal variations were small, even considering that the studied area is shallow and subject to the action of waves and currents.

Carbonate contents tended to vary within similar intervals for each station. In the sediments from stations 1 and 2, $CaCO_3$ contents were between 5% and 10%, but in the summer 1999 the carbonate percent in the sediment from station 1 was low (2%). Sediments from stations 3 and 5 exhibited more carbonates (above 10%), whereas in station 4, the percent was usually low.

The TOC contents were more variable in the sediments from stations 1 and 2, while in the sediments from stations 3, 4 and 5 the TOC content variations were low. The higher values were found close to the sewage diffusers (station 1), indicating influence of the discharges on the organic enrichment. For the presence of total S, there were small temporal variations in sediments from stations 2 and 4, which had low levels of total S. The highest variation was observed in the sediments from station 3. Moderate levels were observed in station 5, whereas the sediment from station 1 had consistently higher concentrations, possibly due to the sewage discharge. The total N content showed little variation over time for a particular station: higher levels were observed in sediments from stations 1, 3 and 5 and lower levels occurring in sediments from stations 2 and 4.

With regards to the metals distribution, sediments from station 1 exhibited the highest concentrations during the summer and winter 1999, whereas sediment from station 5 had the highest levels in the summer 2000. The other stations exhibited low variability. Control sediment tended to exhibit higher levels of Al, Fe, Ni, Co and Zn, however it is not possible to know if this is due to natural causes or human contributions.

For the MBAS, values tended to be similar over time. Sediments from station 1 tended to have the highest concentrations; however in the summer 1999, a high concentration was observed for the control. This result suggests that the control station may be receiving contaminants.

Results observed in the toxicity tests were more variable. Sediments from station 1 were toxic in the first three campaigns, whereas sediments from station 5 were toxic in winter 1998 and summer 1999. The samples collected at station 2 did not produce significant mortality in the conducted tests. Toxicity was also observed at station 4 in 1998 and 2000. The sediments from station 3 were toxic in all tests, except in the winter 1999.

5. Discussion

In Brazil, the oceanic disposal of urban effluents by sewage outfalls has been considered a satisfactory option, in terms of economics and beach sanitation (Agudo, 1983; Occhipinti, 1972; Tommasi, 1987a,b). It was adopted in several coastal cities, such as Fortaleza, Salvador, Belém, Rio de Janeiro, Niterói, Porto Alegre and Vitória (Rachid, 2002) in hopes of eliminating problems of microbiological contamination on beaches. Other than those effluents which are chlorinated, no other treatment has been applied to these effluents. These discharge practices are based on the assumption that marine water bodies can assimilate contaminants without any detrimental environmental effects (Gonçalves and Souza, 1997). The first step in understanding the influence of sewage on sediment quality is a knowledge of the local sediment characteristics and the hydro-dynamic processes related to particles precipitation, re-suspension and sediment transport.

According to Ponçano (1985), sedimentation in the Santos Bay "is the product of the influence of both continental and marine processes, which interact producing a complex pattern". Studies available for Santos Bay show that, before the operation of the oceanic disposal system, the region was divided in two sectors: one towards the east, with silty sediments; and one towards the west, with sandy sediments (Fúlfaro and Ponçano, 1976; Fúlfaro et al., 1983; Ponçano, 1985; Tommasi, 1979). Finer sediments appeared to be transported eastward, especially during the winter (Ponçano, 1985). Recent studies suggested that coastal waters flow into the bay along the bottom, (Harari and Camargo, 1997; Harari et al., 2000), corroborating the previous reports.

Other recent investigations have shown that the previously described patterns were kept, but in the central portion of the bay, close to the outfall diffusers, the sediments were finer and organically more enriched (Bonetti, 2000; FUNDESPA, 1999). Braga et al. (2000) showed that the water around the diffusers were rich in nutrients, suggesting that the sewage discharge could be the possible cause of the sediment organic enrichment. The results obtained in the present study followed the historical pattern for Santos Bay, especially the more recent studies. Sediments from station 1 were always fine and rich in total N, S and TOC, showing that the sewage discharge is sufficient to alter some sediment properties. At this station, levels of S reached 198 times the lower observed concentrations during the summer 1999. Moreover, TOC and nutrient enrichment were also detected at sediments from station 5, which follows predictions from the models for sediment transport previously mentioned. A study recently conducted in Santos using the sediment quality triad (Abessa, 2002) found similar results for enrichment in the vicinity of the diffusers, and using interpolation suggests that its direct influence occurs up to 1 km from the discharge. Our results are in agreement with those findings.

The precipitation of solids present in the sewage around the diffusers is expected in oceanic disposal systems, as part of the depuration process (Gonçalves and Souza, 1997). According to Rachid (2002) the concentration of suspended solids in the effluent of Santos is high, being considered above the average for urban sewage. This information provides important evidence of the potential for sewage to influence the grain size distribution and increase the organic richness in the vicinity of the diffusers. Modifications in the grain size distribution and nutrients levels may cause alterations of the structure of the benthic community, and should be further investigated. Moreover, many contaminants present in effluents are adsorbed onto the particles (Burgess and Scott, 1992), and sink to the bottom with them, as observed by Matthai and Birch (2000) in sediments situated around sewage outfalls from Australian East Coast.

In the present study, chemical analyses were only made for the campaigns conducted in 1999 and 2000. The concentrations of metals tended to be low (<TEL) for the most of the analyzed elements. Concentrations above the TEL were observed for Hg and Ni, with higher concentrations for sediments from station 1 (1999) and 5 (2000). In the sediments from station 4, levels of Hg exceeding the TEL were observed in 1999 and 2000. Occasional TEL exceedences were also observed for Cd (stations 1 and 5) and Cr (stations 1 and 2). For the sediments from Santos, Abessa (2002) analyzed the relationship between toxicity and the contamination levels proposed by Canadian Sediment Quality Guidelines, and concluded that when TEL levels are exceeded, sediments have a high probability of being toxic. The present and the other recent studies (Bonetti, 2000; Lamparelli et al., 2001) indicate higher levels of metals than those observed in the past (Boldrini and Navas-Pereira, 1987; CETESB, 1985; Tommasi, 1979), which suggests that there is a historical tendency of increasing concentrations of metals in the sediments. However, along the 3 campaigns evaluated in this paper, the increase was not detected suggesting that such increases occur on a larger time scale than that considered in the present study. Although metals concentrations have not been particularly elevated, the Ni and Hg levels indicate that the sewage is contaminating the sediments. This is particularly important because the Santos Bay is an important shrimp fishing site for local fishermen. Therefore, if the objectives are to control or mitigate the possibility of environmental risks, the contamination process should be known so that the sources can be controlled.

According to Gonçalves and Souza (1997), sewage has a typical composition, with high contents of solids and nutrients and low concentrations of metals, hydrocarbons and pesticides, but this is not always the case (Gonzalez et al., 1999). Matthai and Birch (2000) observed high concentrations of metals in the effluents discharged by the outfalls of Malabar, Bondi and North Head, all them situated in Sydney. Urban sewage in Santos may be a mixture of domestic and hospital effluents, storm water, residues from commercial offices, gas stations and small industries.

The effluent discharged by the Santos sewage outfall was chemically analyzed by Rachid (2002). The concentrations of metals, PCBs, organochlorines and PAHs were very low, and for some contaminants the levels were below the detection limits (Table 10). Contents of solids, ammonia, sulfides and oils and greases were high, exceeding the limits established for the Brazilian emission limits (Brasil, 1986). The result of this chemical analysis seems to be incompatible with the Ni and Hg levels observed in the sediments. Important information which could explain this difference was obtained by Rachid (2002). This author evaluated the effluent toxicity using the Toxicity Identification and Evaluation (TIE) approach.

Table 10
Composition of the effluent discharged by the Santos submarine sewage outfall (from Rachid, 2002)

Parameter	Result	Maximum limit (Brasil, 1986)	Parameter	Result	Brazilian limit (Brasil, 1986)
Metals (mg/l)			*Aromatics (μg/l)*		
Ar	<0.02	0.5	Benzene	<2.50	–
Cd	0.008	0.2	Etilbenzene	<2.50	–
Cu	0.05	1.0	Toluene	16.5	–
Cr hexavalent	<0.02	0.5	Xilene	<2.50	–
Es	<1.1	4.0	*Others (mg/l)*		
Fe soluble	0.17	15.0	Bo	0.24	5
Mn	0.09	–	Ca	44.8	–
Hg	< 0.002	0.01	Chlorides	383	–
Ni	<0.04	2.0	DBO	210	–
Ag	< 0.005	0.10	DQO	715	–
Se	<0.02	0.05	Phenols	0.24	0.5
Zn	0.38	5.0	Fluorides	<5.00	10
Pb	<0.1	0.5	NH_3–NH_4	54.9	5
Halogenated hydrocarbons (μg/l)			Total N	74.1	–
PCB	ND	–	Oils and greases	236	70
Aldrin	ND	–	K	20.6	–
BHC	ND	–	Sulfides	1.93	1
DDE	ND	–	*Solids (mg/l)*		
DDT	ND	–	Total filtered residue	880	–
Endosulfan	ND	–	Fixed residue	770	–
Endrin	ND	–	Fixed not filtered residue	150	–
Heptachlor	ND	–	Total not filtered residue	730	–
Heptachlor epoxide	ND	–	Volatile not filtered residue	580	–
HCB	ND	–	Total residue	1610	–
Lindane	ND	–	Volatile residue	840	–
Methoxichlor	ND	–			
Mirex	ND	–			
TDE	ND	–			
Toxaphene	ND	–			

The effluent toxicity was high, with EC50 <10% dilution. After the pre-conditioning process, the toxicity was higher, indicating that any process inside the Plant was responsible for the toxicity increasing, and the chlorination was suspected. The TIE indicated that the contaminants responsible for the observed toxicity were the suspended solids, ammonia, the volatile compounds and the non polar organics.

The contribution of suspended solids to the effluent toxicity suggests that the contaminants are adsorbed to the particles, as could be expected (Burton, 1992). As previously mentioned (Rachid, 2002), the sewage from Santos has a high suspended solids content, the majority of which tends to precipitate quickly around the diffusers, as indicated by the sediment grain size distribution analyses. Thus, contaminants from the effluent appear to be transferred to the sediments via precipitated particles. The analysis of chemicals present on the suspended solids could confirm this hypothesis. Regardless, the removal of suspended solids from the effluent should be encouraged, as the current levels exceed the Brazilian standards.

It is recommended that the dispersal modeling for the dilution of sewage disposed into the sea by this system be reevaluated, considering the different "behavior" between dissolved contaminants and those sorbed onto particles. According to Marcellino (2000), the sewage outfall of Santos operates under proper conditions for diluting the effluent and microbial decomposition. However, the present investigation shows that the precipitation of particles to the bottom cannot be considered a depuration process, if the sediments are accumulating contaminants.

The presence of some metals in sediments from station 5 during the Summer 2000 may be due to a patchy distribution (Fúlfaro et al., 1983; Krumgalz et al., 1989) or to remobilization and transport processes, which occur eastward (Ponçano, 1985). This phenomenon was observed previously in Cuba (Gonzalez et al., 1999) and Croatia (Ujevic et al., 1998). Data obtained in the present study are not conclusive for this topic, showing the need for confirmatory studies.

In addition to metals, detergents are present in sewage as well (Field et al., 1995; Marcomini et al., 1987; Swedmark et al., 1971), and can accumulate in the sediments (Fytianos et al., 1998; Stoll et al., 1997). In this study, higher contents of MBAS were found only in the sediments from station 1, situated close to the outfall diffusers. In the other stations, the MBAS levels were low, similar to those found in the same area before the sewage outfall operation. The MBAS concentrations at station 1 sediments were similar to those observed by Tommasi (1979) in the past, at the inner portion of the Santos Estuary, which used to receive contaminated waters from the metropolitan region of São Paulo, through the Henry Bornen Electric Plant (now inactivated). A study conducted by Medeiros (2000) showed that the Linear Alkyl Benzenes distribution near the sewage outfall of Santos follows the same pattern observed in the present study.

Although sediment contamination by detergents is not considered to be a contaminant of concern for Santos Bay, these compounds can cause toxic effects to resident biota (Mastroti et al., 2001). Unfortunately, the MBAS concentrations in the effluent were not estimated by Rachid (2002), but in a recent study (Bosquilha, 2002), detergents were measured in levels ranging from 0.15 and 0.26 mg/l in the bottom water close to the diffusers. These concentrations are considered toxic to sea-urchin embryos (Mastroti et al., 2001). Moreover, these authors demonstrated that the biodegradability of detergents in seawater is low.

The accumulation of contaminants in the sediment may produce toxicity on the benthic biota and threaten the ecosystem balance. Beyond the presence of metals and detergents in the sediments, an additional contribution to the toxicity can be due to the high concentrations of sulfides and ammonia, which were present in high concentrations in sediments from the studied area (Abessa, 2002). Possibly, the toxic effects observed on *T. viscana* survival were caused by the combination of the contaminants mentioned above. This possibility is still supported by the negative correlations between amphipod survival and some variables, as % mud and total N, and levels of Ni and Hg.

6. Conclusions

The toxicity observed in the present study was similar to that reported previously in the same area (Abessa et al., 2001) and in the vicinities of other sewage outfalls from the State of São Paulo (Abessa and Sousa, 2001). The hypothesis of seasonal variation on the toxicity could not be totally confirmed in the present study. Variations in the number of toxic samples were observed between 1999 and 2000, with decreasing sediment quality in the summer, but this tendency was not very clear. This fact supports the necessity of continuing the environmental monitoring around the Santos sewage outfall diffusers.

The sewage outfall of Santos is a source of alterations to the sediment from the central area of the Santos Bay, causing changes in its granulometric, chemical and ecotoxicological characteristics. Although these modifications appear to be localized, mainly in the vicinity of the diffusers, the transport of sediments to other sectors of the bay appears to occur, thus the influence of the discharge may comprise a broader area than was investigated in the present study.

The modifications in sediment quality and the exceedence of Brazilian standards for certain effluent constituents indicate that additional sewage treatment should be installed in the Santos Plant, especially to reduce the levels of suspended solids.

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