

Turnbull, D. A. (1979). The water quality characteristics and distribution of benthic invertebrates in a polluted harbour, Barbados, West Indies. M.Sc. thesis, McGill University, Montreal, Canada.

Veziņa, R. R. (1975). Seawater quality and phytoplankton of inshore waters of Barbados: a study of the effects of organic pollution in a tropical environment. M.Sc. thesis, McGill University, Montreal, Canada.

Wade, B. A. (1971). Marine pollution problems in Jamaica. *Mar. Pollut. Bull.* 2, 29–30.

Wade, B. A. (1976). The pollution ecology of Kingston Harbour, Jamaica. Research report from the Department of Zoology, University of the West Indies, Mona, Jamaica.

Zar, J. H. (1984). *Biostatistical Analysis*. Prentice-Hall, Inc., Englewood Cliffs.

Nutrients, Heavy Metals and Organic Micropollutants in an Eutrophic Brazilian Lagoon

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This article documents the environmental quality with respect to nutrients, heavy metals, and organic micropollutants at Lagoa de Guarapina, a tropical eutrophic lagoon of Rio de Janeiro State, Brazil. Concentrations of nutrients and heavy metals in the lagoon and its tributaries were low, closely resembling natural conditions. However, Pb formed the exception, and its presence in conjunction with detectable concentrations of organic micropollutants suggest that minor pollution effects are occurring via atmospheric inputs.

The Fluminense coastline between the cities of Rio de Janeiro and Cabo Frio includes numerous eutrophic lagoons. Fishing and recreation are the main human activities, but a recent increase in urbanization has resulted in uncontrolled effluent discharges into some of these lagoons. Concern about their water quality status has only now led to implementation of baseline studies and coastal management strategies in the region.

Guarapina Lagoon (22° 56' S, 42° 42' W) forms part of the Marica lagoon system which lies approximately 50 km east of Rio de Janeiro city. It represents the most seaward lagoon of the system, which consists of four interconnected shallow lagoons, with a surface area of 6.5 km², a mean depth of 1 m, and a connection to the sea via a long, narrow channel. It is a poorly flushed lagoon with a mean residence time of water of around 1.5 months (Kjerfve *et al.*, in press). The lagoon is mesotrophic in winter and eutrophic in summer (Machado & Knoppers, 1988).

The drainage basin is sparsely populated, subject to some deforestation and agricultural land use, and

industries are absent. The main sources of allochthonous matter are three rivulets which drain into a small estuary at the northern section of the lagoon, the adjacent lagoon system at the western side, and the bordering macrophyte vegetation. The mean annual rainfall of the region is 1300 mm (Barbieri, 1986).

The present study reports on nutrients, heavy metals, and organic micropollutants concentrations in the Guarapina Lagoon system to evaluate its present environment quality and to provide baseline data for further monitoring of these variables.

Material and Methods

Sampling for dissolved inorganic nitrogen species (ammonia, nitrite, and nitrate), orthophosphate (PO₄-P), and chlorophyll *a* (Chl. *a*) was conducted over an annual cycle (winter 1985–1986) at more or less fortnightly intervals in the rivulets, at four stations in the lagoon (upper and lower estuary, central and lower region, at the channel connection with the adjacent lagoon, and sporadically in the coastal water. In addition, samples for particulate organic carbon (POC) and nitrogen (PON) were collected at the central station in the lagoon. Samples were collected with a Van Dorn PVC type water bottle and kept on board on ice in the dark, and filtered 3 h later over pre-combusted GF/C filters prior to analysis. Nutrient analyses were carried out according to Grasshoff *et al.* (1983), in accordance with the detection limits cited therein, with the exception of ammonia at 0.4 μM. Chlorophyll *a* was determined as in Strickland & Parsons (1972) and POC and PON with a Hewlett-Packard 185B CHN-Analyser after acidification of the filters with 0.1 N HCl. The POC and PON analyses were carried on at

the Institute of Marine Sciences, University of Kiel, FRG.

Trace metal analyses were performed on surficial sediments at five stations (higher, middle, and lower estuary, central lagoon, and lower lagoon, close the tidal inlet) and their vertical distribution was assessed on a separate sediment core from the central lagoon station. Trace metals from surficial (0–5 cm) sediments, fraction <63 μ m were extracted by acidic digestion in Teflon bombs and analysed with a Baird Atomic 3400 Atomic Absorption Spectrophotometer (AAS) with Deuterium background correction. Detection limits of heavy metals were as follows: Mn>0.01, Cr>0.2, Cu>0.05, Ni>0.05, Pb>0.15, and Zn<0.05, μ g g⁻¹ of dried sediment. Analysis of reference material, International Atomic Energy Agency (IAEA) 'Marine Sediment', indicate data quality (Table 1). The content of organic matter was obtained via sediment combustion at 450°C for 12 h and the cation exchange capacity (CEC) was measured via the ammonium acetate method as in Jackson (1958). Trace metal analyses on the sediment core were carried out on a Bausch & Lomb ARL emission spectrometer model 3500 OES, equipped with ICP, in the Geochemical Laboratory, University of Mainz, FRG. The analyses were carried out on total sediments. Organic micropollutants (PHAs, PCBs, 'drins', DDT, DDD, and DDE) were analysed from a sediment core at the central lagoon station. Polyaromatic hydrocarbons were determined by GC/MS and chlorinated contaminants by GC/ECD according to Japenga *et al.* (1987). These analyses were carried out at the Institute of Soil Fertility, Haren, The Netherlands.

Results and Discussion

Table 2 gives the mean concentration and standard deviation for total dissolved inorganic nitrogen (TIN=NH₃-N+NO₂+NO₃-N), orthophosphate, chlorophyll *a*, and salt (S‰) at the sampling sites

TABLE 1

Concentrations of heavy metals in reference material, International Atomic Energy Agency (IAEA) 'Marine Sediments' compared with certified values in μ g g⁻¹ dried sample.

	Cu	Pb	Zn	Ni	Cr	Mn
Certified Value	72.2	120	439	31	149	777
This Study	85 ± 5	134 ± 16	508 ± 26	38 ± 4	122 ± 13	820 ± 21

between the fluvial and marine end-members. The fluvial, marine, and adjacent lagoon sources exhibited higher nutrient concentrations than the estuarine, central, and lower portions of the lagoon. Nitrate was the major component of TIN in the fluvial and marine sources, whereas ammonia predominated at the adjacent lagoon source and within the lagoon. The lagoon thus serves as a major sink to nutrients. Nutrient input from the fluvial sources is considered to be natural or quasi-natural as land usage is mainly restricted to some cattle pastures and crop growth without the use of fertilizers and ammonia input from the adjacent lagoon originates primarily from the degradation of the benthic algae *Cladophora* sp. (Moreira, 1988). The low nutrient concentrations in the lagoon are primarily the result of incorporation by phytoplankton primary production which reaches 370 g m⁻² yr⁻¹ (net) (Moreira, 1988, Machado & Knoppers, 1988) and subsequent storage in autotrophic biomass and detritus of phytoplankton origin (Knoppers & Moreira, in press) as corroborated by the annual range of POC of 2.76 to 13.15 mg l⁻¹, the low mean annual C:N ratio by weight of 5.92 ± 1.12 (n=17) for the central lagoon, and the chlorophyll *a* values shown in Table 2.

Intra- and interspecific variability in nutrient concentrations for the majority of the homogeneously mixed shallow and quasi-unperturbed sub-tropical and tropical lagoons lies within a range 0.3–3 μ M for PO₄-P and 1–8 μ M for TIN (Beers & Herman, 1969, Day *et al.*, 1982, 1988, Halin & Guerguess, 1981, Hodgkin & Lenanton, 1981, Knoppers & Opitz, 1984, Mandelli, 1981, Mee, 1977, Nixon, 1982, Okuda, 1981, Tundisi, 1973, Vaultot & Frisoni, 1986). This range excludes extreme nutrient concentrations caused by the short term input of pore-water nutrients from re-suspended sediments. In Guarapina, fluvial and water-column nutrient concentrations were at the lowest levels of the overall range recorded for other lagoons and may thus represent background levels for tropical and sub-tropical lagoons which further harbour drainage basins with restricted land use.

Table 3 shows the horizontal distribution of salinity, the cation exchange capacity (CEC) and organic matter (OM) content, and heavy metals from surficial sediments in the lagoon. The CEC, OM and the heavy metals Mn, Cr, Zn, and Pb generally decrease from the fluvial to the lower estuarine station, with maximum values at the central lagoon station and decrease sharply towards the lower portion, close to the tidal inlet. Cu and Ni however, remained fairly constant

TABLE 2

Mean values and standard deviations of salinity (S‰), orthophosphate (PO₄-P), total inorganic nitrogen (TIN), and chlorophyll *a* (Chl. *a*) of sampling stations in Guarapina Lagoon (n = number of measurements).

Station	S (%)	PO ₄ -P (μ M)	TIN (μ M)	Chl. <i>a</i> (μ g dm ³)	n
Fluvial (rivulet)	0	1.14 ± 0.81	6.52 ± 4.0	5.3 ± 3.5	23
High estuary	1.4 ± 1.7	0.96 ± 0.78	2.46 ± 1.0	6.3 ± 3.8	16
Low estuary	13.7 ± 2.9	0.28 ± 0.24	1.31 ± 1.2	20.1 ± 15.9	24
Control lagoon	17.7 ± 2.1	0.35 ± 0.20	1.78 ± 0.8	43.4 ± 31.8	22
Lower lagoon	18.8 ± 2.3	0.35 ± 0.21	3.30 ± 4.1	36.9 ± 27.0	24
Channel to adjacent lagoon	14.5 ± 2.0	0.56 ± 0.40	14.5 ± 14.9	39.6 ± 32.0	9
Sea	34.2 ± 1.2	0.56 ± 0.50	3.1 ± 2.1	3.8 ± 1.3	7

TABLE 3

Organic matter content (OM) (%), cation exchange capacity (CEC) (meq 100 g⁻¹ dry wt) and total metal concentrations (µg g⁻¹ dry wt) in surficial sediments of sampling stations in Guarapina Lagoon. Mean values (\bar{x}) and standard deviations (SD) for metals (n=9) and means of triplicate samples for OM and CEC.

Stations		OM	CEC	Mn	Cr	Cu	Zn	Pb	Ni
High estuary	\bar{x}	15.4	31.9	324	41	25	132	66	38
	SD	-	-	52	8	4	29	21	8
Mid estuary	\bar{x}	11.9	42.1	231	31	28	119	59	33
	SD	-	-	40	12	7	36	17	8
Low estuary	\bar{x}	14.5	28.3	210	22	21	111	43	25
	SD	-	-	38	7	7	33	15	11
Central lagoon	\bar{x}	22.8	42.7	409	43	26	151	80	42
	SD	-	-	53	10	7	39	15	10
Lower lagoon	\bar{x}	12.8	8.8	235	29	23	108	56	28
	SD	-	-	27	13	5	5	26	7

throughout. The dominance of fine pelitic particles, the high OM and CEC of the central lagoon sediments provides an efficient trap for metals which are transported from land via the rivulets (Table 3). Nickel and Cu concentrations are similar to those found in local parental rock in the basin, suggesting that detrital minerals probably carry these two metals in lattice position (Lacerda & Abrao, 1987). The concentrations presented in Table 3 show that, with the exception of Pb, all metals occur in the concentration range of organic-rich, non-contaminated coastal sediments (Lacerda *et al.* 1988). Zn, Cu, and Ni concentrations were lower or equal than the concentrations recorded in Ostion lagoon, a similar and unperturbed lagoon off the coast of the Gulf of Mexico (Paez-Ozuna *et al.*, 1986). In contrast, Pb exhibited higher levels by a factor of two than Coatzacoalcos estuary, a perturbed system at the Gulf of Mexico (Paez-Ozuna *et al.*, 1986), but lower levels than the polluted lower Rhine (Forstner & Patchinellam, 1980), Mazatlan Harbour, Mexico (Paez-Ozuna *et al.*, 1988), Venice Lagoon (Donazzolo *et al.*, 1984) and the bays of Guanabara and Sepetiba, Brazil (Lacerda *et al.*, 1988).

Pachineelam *et al.* (1988) suggested that the above Pb levels in Guarapina lagoon are caused by atmospheric input from industrial sources of Rio de Janeiro metropolitan area. This is corroborated by the marked vertical gradient of the metals Pb and Ni from the core in the central portion of the lagoon (Table 4), which clearly shows an increase in the surface sediments when compared to deeper layers. The presence of Precambrian granitic gneisses, particularly poor in Pb, and the absence of fertilizer usage and industrial activity in the drainage basin indicate that the atmosphere is a possible source. Trindade *et al.* (1981) found high concentrations of heavy metals in atmospheric particles around the industrial districts of Rio de Janeiro. Prevailing SE winds during autumn, winter, and spring are probably responsible for the transport of heavy metals to Guarapina lagoon. For the other metals however, evidence of atmospheric input could not be found.

Atmospheric input seems to hold for the organic micropollutants, PCBs and PAHs, typical of industrial origin, detected in the surface layers of sediments at the central lagoon station (Table 5). However, due to the

TABLE 4

Trace metal concentrations in a sediment core from Guarapina Lagoon. Mean values (dry wt) of duplicate samples.

Core depth (cm)	Fe (%)	Cr (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Al (%)	Ni (ppm)
00-02	5.0	50	102	22	88	8.4	25
02-07	5.5	-	122	62	58	8.6	45
07-12	5.8	65	122	28	35	9.2	29
12-22	3.7	35	88	18	7	5.1	16
22-32	4.2	36	96	22	10	5.8	14
32-42	4.7	38	98	25	2	5.1	9
42-52	4.2	32	62	18	2	5.0	2
52-62	5.1	36	76	25	-	5.5	-
62-72	4.9	36	75	23	-	5.1	-
72-82	5.8	40	98	26	2	6.8	-
82-92	5.0	32	87	22	-	6.7	-
92-102	4.7	30	92	18	-	5.8	-

TABLE 5

Organic micropollutants in a sediment core from Guarapina Lagoon. Mean values (dry wt) of triplicate samples.

Core depth (cm)	PCBs (ppb)	PAHs (ppm)	DDT+DDE+DDD (ppm)	'Drins' (ppb)
00-01	9.7	4.9	6.0	1.2
02-04	5.9	9.0	5.8	0.6
06-08	2.1	0.14	3.9	0.2
14-18	1.1	0.12	3.1	0.1

small size of the core and the fact that chlorinated insecticides and DDT have been applied in the early 1950s in the area to control malaria, no conclusion can be drawn as to their role as main sources to the lagoon. Organic micropollutants concentrations are however well below those reported in Guanabara Bay, Brazil (Japenga *et al.* 1988), and Venice Lagoon (Pavoli *et al.*, 1987).

The results indicate that Guarapina Lagoon is a naturally eutrophicated system, but subject to initial stages of anthropogenic pollution of some heavy metals and organic micropollutants of industrial origin via atmospheric deposition.

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Barbieri, E. B. (1986). Distribuicao de pluviosidade ao longo do trecho Niteroi-Cabo Frio, R. J. *Cienc. Cult.* **38**, 766-767.

- Beers, J. R. & Herman, S. S. (1969). The ecology of inshore plankton populations in Bermuda. Part I. Seasonal variation in the hydrography and nutrient chemistry. *Bull. Mar. Sci.* **19**, 253-278.
- Day, R. H., Barreiro, M. T., Ley-Lou, F. & Madden, C. J. (1982). Primary production in the Laguna de Terminos, a tropical estuary in the southern Gulf of Mexico. *Oceanologica Acta* **5**, 269-276.
- Day, J. W., Madden, C. J., Ley-Lou, F., Wetzel, R. L. & Navarro, A. M. (1988). Aquatic primary productivity in Terminos Lagoon. In *Ecology of Coastal Ecosystems in the Southern Gulf of Mexico: The Terminos Lagoon Region*. (A. Yanez-Arancibia & J. W. Day, eds), pp. 221-235. Universidad Nacional Autonoma de Mexico, Mexico.
- Donazzolo, R., Orio, A. A., Pavoni, B. & Perin, G. (1984). Heavy metals in the sediments of the Venice Lagoon. *Oceanologica Acta* **7**, 25-32.
- Forstner, U. & Patchineelam, S. R. (1980). Chemical associations of heavy metals in polluted sediments from the lower Rhine river. *Adv. Chem. Am. Chem. Soc.* **189**, 177-193.
- Grasshoff, K. M., Ehrhardt, M. & Kremling, K. (Eds.) (1983). *Methods of Seawater Analysis*. Verlag Chemie, Weinheim.
- Halin, Y. & Guerguess, S. K. (1981). Coastal lakes of the Nile delta. Lake Menzalah. Unesco Tech. Pap. *Mar. Sci.* **33**, 135-172.
- Jackson, M. L. (1958). *Soil Chemical Analysis*. Prentice Hall, Eaglewood Cliffs, N.J.
- Japenga, J., Wagenaar, W. J., Smedes, F. & Salomons, W. (1987). A new, rapid, clean-up procedure for the simultaneous determination of different groups of organic micropollutants in sediments, application to two European sediment studies. *Environ. Technol. Lett.* **8**, 9.
- Japenga, J., Wagenaar, W. J., Salomons, W., Lacerda, L. D., Patchineelam, S. R. & Leitao Filho, C. M. (1988). Organic micropollutants in the Rio de Janeiro coastal region, Brazil. *Sci. Tot. Environ.* **75**, 249-259.
- Kjerfve, B., Knoppers, B. A., Moreira, P. F. & Turcq, B. (1990). Hydrological regimes in Lagoa de Guarapina, a shallow Brazilian coastal lagoon. *Acta Limnol. Bras.* **3** (in press).
- Knoppers, B. A., Opitz, S. S., Souza, M. P. & Miguez, C. F. (1984). The spatial distribution of particulate organic matter and some physical and chemical water properties in Conceicao Lagoon, Santa Catarina, Brazil. *Arch. Biol. Tecnol.* **27**, 59-77.
- Knoppers, B. A. & Moreira, P. F. (1988). The short term effect of physical processes upon nutrients, primary production and sedimentation in Guarapina Lagoon, Brazil. *Acta Limnol. Bras.* **2**, 405-430.
- Knoppers, B. A. & Moreira, P. F. (1990). Materia em suspensao e sucesso do fitoplankton na Lagoa de Guarapina. RJ. *Acta Limnol. Bras.* **3** (in press).
- Lacerda, L. D. & Abrao, J. J. (1987). Nickel geochemistry in sediments of a naturally eutrophicated coastal lagoon. *Cienc. Cult.* **39**, 186-188.
- Lacerda, L. D., Souza, C. M. M. & Pestana, M. H. D. (1988). Geochemical distribution of Cd, Cu, Cr and Pb in sediments of estuarine areas along the southeastern Brazilian coast. In *Metals in Coastal Environments of Latin America* (U. Seeliger, L. D. Lacerda & S. R. Patchineelam, eds.), pp. 86-99. Springer-Verlag, Berlin.
- Machado, E. C. & Knoppers, B. A. (1988). Sediment oxygen consumption in an organic rich subtropical lagoon, Brazil. *Sci. Tot. Environ.* **75**, 341-349.
- Mandelli, E. F. (1981). On the hydrography and chemistry of some coastal lagoons of the Pacific Coast of Mexico. Unesco Tech. Pap. *Mar. Sci.* **33**, 81-117.
- Moreira, P. F. (1988). Ciclo anual de nutrientes e producao primaria na Lagoa de Guarapina. RJ. M.Sc. Thesis. Univ. Fed. Fluminense, Niteroi.
- Nixon, S. W. (1982). Nutrient dynamics, primary production and fisheries yields of lagoons. *Oceanologica Acta* **5**, 357-371.
- Okuda, T. (1981). Inorganic and organic nitrogen contents in some coastal lagoons of Venezuela. Unesco Tech. Pap. *Mar. Sci.* **33**, 119-134.
- Osuna-Lopez, J. I., Ortega-Romero, P. & Paez-Ozuna, F. (1986). Cd, Co, Cr, Cu, Fe, Ni, Pb y Zn en los sedimentos del Puerto y antepuerto de Mazatlan. *Cienc. Mar.* **12**, 31-39.
- Paez-Ozuna, F., Botello, A. V. & Villanueva, S. (1986). Heavy metals in Coatzacoalcos estuary and Ostion lagoon, Mexico. *Mar. Pollut. Bull.* **17**, 516-519.
- Pavoni, B., Sfriso, A. & Marcomini, A. (1987). Concentration and flux profiles of PCBs and DDTs in a dated sediment core from lagoon of Venice. *Mar. Chem.* **21**, 25-36.
- Patchineelam, S. R., Leitao Filho, C. M., Kristokakis, K. & Tobshall, H. J. (1988). Atmospheric lead deposition into Guarapina lagoon, Rio de Janeiro State, Brazil. In *Metals in Coastal Environments of Latin America* (U. Seeliger, L. D. Lacerda, & S. R. Patchineelam, eds), pp. 65-76. Springer-Verlag, Berlin.
- Strickland, J. D. H. & Parsons, T. R. (1972). A practical handbook of seawater analysis. *Bull. Fish. Res. Bd. Can.* **122**, 1-172.
- Trindade, H. A., Pfeiffer, W. C., Oliveira, A. E., Londres, H. & Costa-Ribeiro, C. (1981). Concentrações atmosfericas de total de particulas em suspensão e metais na cidade do Rio de Janeiro. *Cienc. Cult.* **33**, 996-1005.
- Tundisi, J. G., Tundisi, T. M. & Kutner, M. (1973). Plankton studies in a mangrove environment VIII. Further investigations on primary production, standing stock of phyto and zooplankton, and some environmental factors. *Int. Rev. Ges. Hydrobiol.* **58**, 925-940.
- Vaulot, D. & Frisoni, G. F. (1986). Phytoplankton productivity and nutrients in five Mediterranean lagoons. *Oceanologica Acta* **10**, 57-63.