

ORGANIC MICROPOLLUTANTS IN THE RIO DE JANEIRO COASTAL REGION, BRAZIL

J. JAPENGA, W.J. WAGENAAR and W. SALOMONS

*Institute for Soil Fertility/Delft Hydraulics Laboratory, P.O. Box 30003, 9750 RA Haren (Gr)
(The Netherlands)*

L.D. LACERDA, S.R. PATCHINEELAM and C.M. LEITÃO FILHO

Departamento de Geoquímica, Instituto de Química, Universidade Federal Fluminense, Outeiro de S. João Batista, 5º andar 24.210, Centro, Niterói (Brazil)

ABSTRACT

Sediment samples from two protected bays and a lagoon with different environmental characteristics in the Rio de Janeiro coastal area (Brazil) were analyzed for four groups of hydrophobic organic micropollutants: PAHs, PCBs (both of industrial origin), DDT derivatives and Drins (chlorinated pesticides). Differences in contamination levels of the three studied areas reflect the different land use in the vicinity of the examined bays and lagoon: the presence of cities, industries or agricultural activities. A comparison of the contamination of the Rio de Janeiro coastal area with the contamination in the North Sea (Europe) indicates lower levels for the industrial pollutants (PCBs, PAHs) in the Brazilian samples; chlorinated pesticide levels are comparable in both sampling areas.

INTRODUCTION

The Rio de Janeiro coastal region has witnessed a huge increase in urban population during the last decades, accompanied by very rapid growth of industrial and agricultural activities, a development which has probably resulted in a substantial increase in contamination by various groups of pollutants, including hydrophobic organic micropollutants. The most likely environmental compartment for detecting the accumulation of organic micropollutants is the sediment of the numerous coastal lagoons and protected bays which drain the surrounding area; the micropollutants may enter the food chain via biota living on the sediments. This work surveys the levels of contamination with organic micropollutants in two bays and a lagoon with different environmental characteristics in the Rio de Janeiro coastal region. It represents the first study of organic micropollutants in Brazilian sediments.

The following groups of hydrophobic organic micropollutants were studied.

PAHs

Polyaromatic hydrocarbons generally result from the incomplete combustion of organic carbon containing material. Environmental input rates

of PAHs are normally related to urban population density (combustion of household garbage, gasoline, etc.) and the density of coal and oil based industries. The introduction of PAHs into the environment normally occurs through the air (adsorbed onto aerosol particles and in the vapor phase), which is quite polluted in the atmosphere above the city of Rio de Janeiro (Miguel, personal communication, 1987). After wet and dry deposition, various transport processes occur, with the most important final sink for PAHs being sediments.

PCBs

Polychlorinated biphenyls are used as a dielectric insulating fluid in major transformers and capacitors. Their introduction into the environment mainly occurs through direct discharge of industrial effluents and occasionally through leaks from electrical installations and through accidental discharge.

Chlorinated pesticide residues

The introduction of chemically persistent chlorinated pesticides (DDT derivatives, Drins) into the environment depended, until recently, largely upon the intensity and type of agricultural activities. Presently, the use of DDT for agricultural purposes is prohibited in Brazil, but the chemical is still available for the control of malaria and other diseases transmitted through insects and therefore continues to be introduced into the environment; illegal use in agriculture, although not proven, might also introduce substantial amounts of DDT derivatives into the environment.

SAMPLING SITES

Sampling sites were selected mainly based on their different environmental characteristics. For example, the population density in the vicinity of the bay

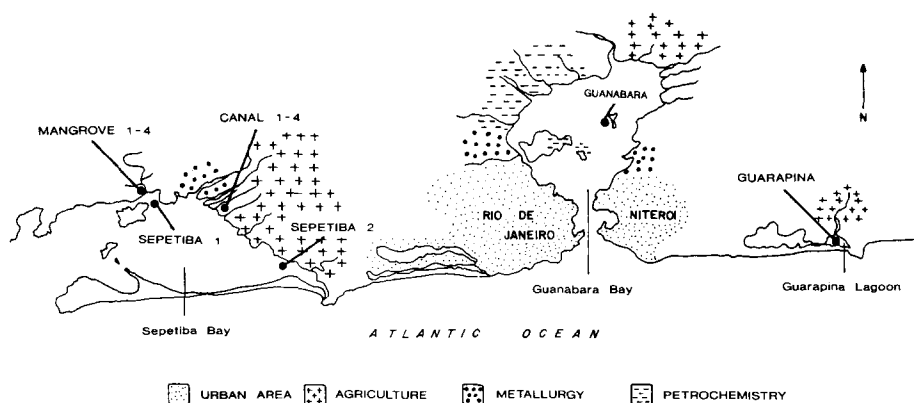


Fig. 1. Map of the Rio de Janeiro sampling area,

or lagoon, the intensity and character of industrial activities and the presence of large-scale agriculture. Figure 1 is a map of the Rio de Janeiro coastal region showing the sampling sites; general characteristics of the different areas, as well as a description of the physical structure of individual samples are presented below.

Sepetiba Bay

Sepetiba Bay is an almost enclosed bay, situated 40 miles west of the city of Rio de Janeiro in a moderately populated area, characterized by the presence of metallurgical industry and intensive agriculture (legumes and fruits).

Samples were collected from a mangrove forest near the Itingussu River (grab samples: Mangrove 1-4) and along the coast, some miles east of the mangrove forest (core sample: Sepetiba 1). Additional samples were collected from rivers and canals draining the agricultural area (grab samples: Canal 1-4) and from Sepetiba Bay itself, from an area where suspended matter, transported by the canals and rivers into the bay, is finally deposited (core sample: Sepetiba 2).

Grab samples from all sites contained finely divided sediment with varying organic carbon content (0.9-9.3%; mean 3.9%). Core sample Sepetiba 1 consisted of a fine particle sediment layer of ~25 cm resting on a coarse sandy lower layer; core sample Sepetiba 2 consisted of fine grain sediment down to at least 60 cm depth.

Mean sedimentation rates in Sepetiba Bay are ~1.3 cm year⁻¹ (Patchineelam et al., 1988).

Guanabara Bay

Guanabara Bay, an almost enclosed bay near Rio de Janeiro city, is characterized by the presence of metallurgical and petrochemical industries as well as agricultural activities. The bay receives most of the effluents (sewage, etc.) of the city of Rio de Janeiro.

A sample was collected near Paqueta Island (core sample: Guanabara). Physical characteristics of this core sample reveal partially decayed plant material in the upper ~3 cm layer, which becomes gradually mixed with more finely divided material down to ~6 cm depth; below 6 cm the core sample consists predominantly of coarse sand.

Mean sedimentation rates in Guanabara Bay are high (~2 cm year⁻¹) (Wilken et al., 1986).

Guarapina Lagoon

Guarapina Lagoon is a closed lagoon ~40 miles east of Rio de Janeiro city, and is only connected with the sea through a narrow channel. There are no important industrial activities in the vicinity of the lagoon. Agricultural intensity is also limited and the population density is quite low.

A sample was collected from the lagoon (core sample: Guarapina); the core sample consisted of finely divided material with a high constant organic carbon content down to a depth of at least 25 cm.

The sedimentation rate is low ($\sim 0.3 \text{ cm year}^{-1}$) (Patchineelam et al., 1988).

The selection of sampling sites permits a comparison of sedimentation in areas with differing characteristics (related to population stress as well as to intensities of agricultural and industrial activities). Different inputs of hydrophobic organic micropollutants may be expected.

METHODOLOGY

Samples were collected, using a simple hollow polyethylene tube, in shallow water near the coast or near river borders. After cutting core samples to the desired depth, they were stored for 30 days at -10°C before analysis. The homogenized samples were extracted with benzene/hexane and the crude extracts submitted to clean-up and fractionation. Final quantification was achieved by GC/MS analysis for the polyaromatic hydrocarbons and by GC/ECD analysis for the chlorinated contaminants (Japenga et al., 1987). In the following sections the concentrations of groups of contaminants are expressed as the sum of a number of congeners:

PAH:	sum of 11 congeners; three-ring up to six-ring systems, including the congeners of known and suspected carcinogenicity
PCB:	sum of six congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180)
DDT derivatives:	sum of <i>o,p</i> - and <i>p,p</i> -isomers of DDT, DDD and DDE
DRINS:	sum of Aldrin, Dieldrin and Endrin.

As organic micropollutants are generally assumed to adsorb onto the organic fraction of the sediments (Means et al., 1980), all concentrations in finely divided sediment samples are normalized to 10% organic carbon content in order to facilitate comparison between samples from different origin. In the case of sediments with a varied physical structure (for example the different layers of the Guanabara Bay core sample) the correlation between organic matter and the organic micropollutants is probably less unequivocal; here, the concentrations for core sample depth profile evaluation are given as concentrations based on sediment dry weight.

RESULTS AND DISCUSSION

Figure 2 shows general contamination levels for the grab samples from the Mangrove forest (Mangrove 1–4) and the core samples Sepetiba 1, Guarapina and Guanabara. For the core samples, concentrations in the upper 10 cm layer are given in order to enable comparison with the grab samples. All concentrations are normalized to 10% organic carbon.

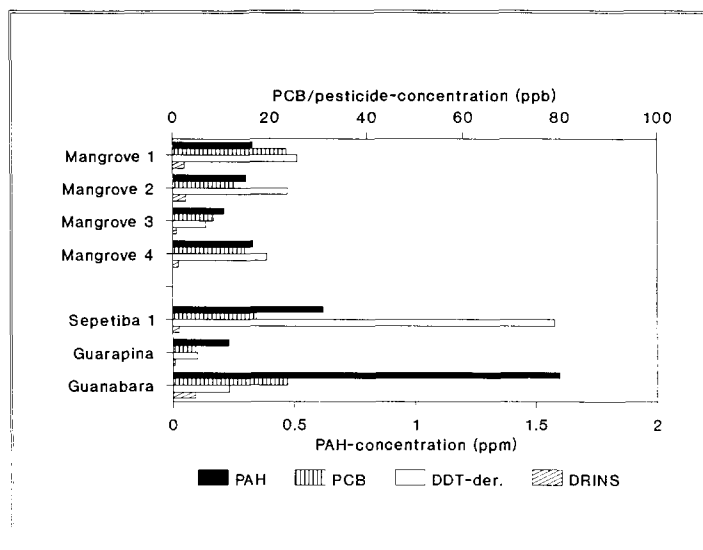


Fig. 2. Organic micropollutant contamination levels in the Rio de Janeiro coastal bays and lagoons.

Contamination levels in Guarapina Lagoon are very low, as expected from the absence of industry, major agricultural activity and large cities in the vicinity. Relatively high levels of DDT are observed in the Sepetiba 1 sample, probably derived from the substantial agricultural area nearby. High levels of

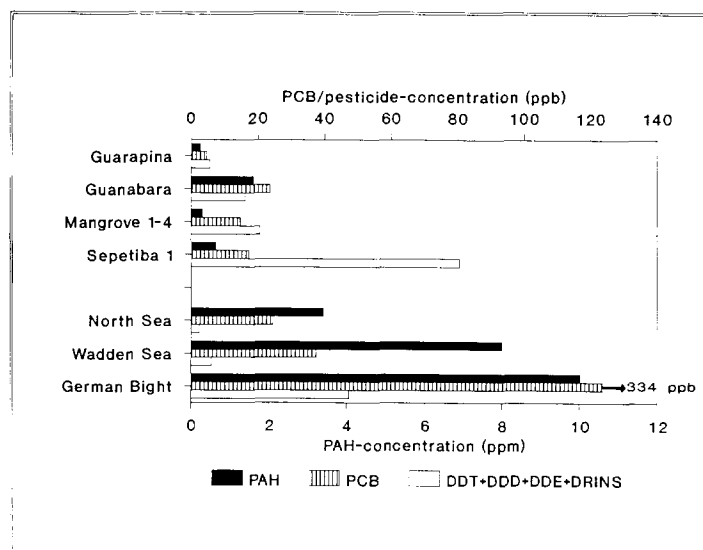


Fig. 3. Organic micropollutant contamination levels in the Rio de Janeiro coastal area and in the North Sea basin.

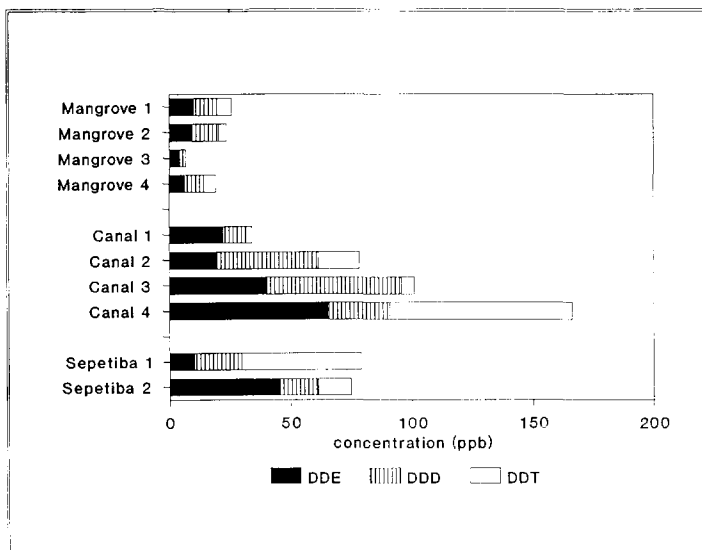


Fig. 4. DDT derivative contamination levels in Sepetiba Bay.

PAHs are found in Guanabara Bay, which may be related to the adjacent Rio de Janeiro city, its airport and the nearby petrochemical industry.

If compared with a European situation, organic micropollutant contamination of the Rio de Janeiro coastal region is not alarming at the moment, as shown in Fig. 3. A comparison is made between the Rio de Janeiro samples (an average value is given for the four mangrove forest grab samples) and three marine sediment samples from the North Sea basin. All concentrations are normalized to 10% organic carbon content. The sample denoted "North Sea" was taken ~50 miles from the Dutch coast and represents the least contaminated of a series of samples taken from the North Sea along the Dutch coast in 1986. This sample may be considered as rather low-polluted in a Western European context. The sample denoted "Wadden Sea" is the average of a number of samples taken from the shallow Wadden Sea lagoon near the Dutch coast in 1985. The "German Bight" sample was taken just outside the River Elbe estuary in 1985 and can be considered as a heavily contaminated marine sediment. It should be noted that samples from main rivers and river estuaries in this area (e.g. the River Rhine and Elbe) are normally even more contaminated with organic micropollutants. The choice of North Sea samples for comparison was based on the fact that analyses of those samples were carried out in the same laboratory and using the same analytical method as for the Rio de Janeiro samples, thereby eliminating intercalibration differences (Japenga et al., 1987; unpublished Report, Delft Hydraulics Laboratory).

Figure 3 shows clearly that concentrations of hydrophobic organic micropollutants of industrial origin (PAH, PCB) are very much higher in the more contaminated North Sea sediments than in the Rio de Janeiro coastal

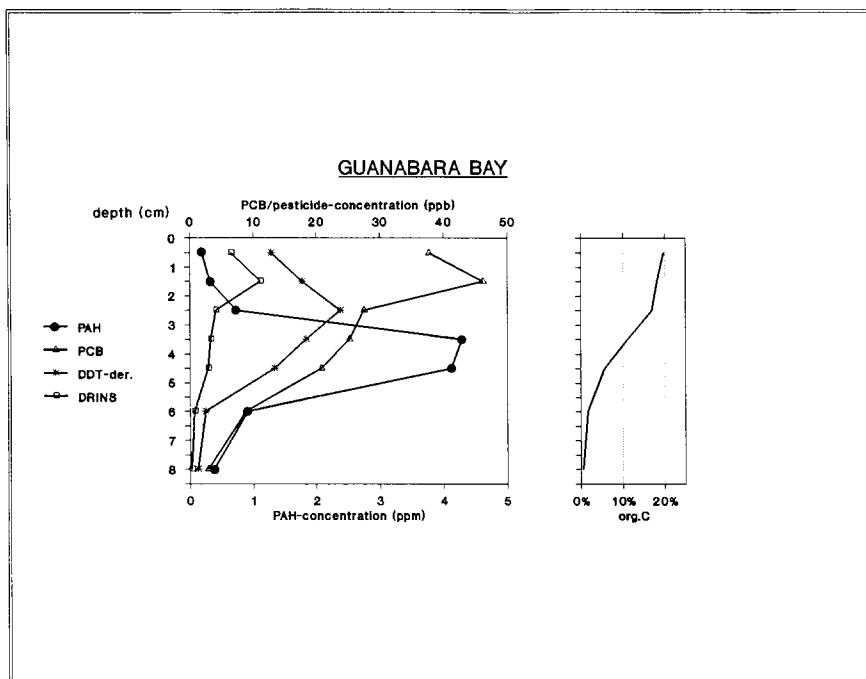


Fig. 5. Guanabara Bay core sample depth profile.

sediments. On the other hand, contamination figures for chlorinated pesticides (mainly DDT derivatives) in the bays and coastal lagoons of the Rio de Janeiro area show levels comparable to the most contaminated coastal sediments from the North Sea and sometimes are even higher.

Also, compared with North American lake and river sediments (Kuntz and Warry, 1983; Onuska et al., 1983), the Rio de Janeiro coastal sediments are much less contaminated with organic micropollutants.

As can be seen from Figs 2 and 3, the Sepetiba 1 sample contained high levels of DDT, which can be attributed to input from the nearby agricultural area. In order to obtain more information about DDT contamination in the Sepetiba Bay region, additional samples from the vicinity of the agricultural area were analyzed: the grab samples Canal 1-4 and the upper 10 cm layer of the core sample Sepetiba 2. The results (all concentrations normalized to 10% organic carbon content) are given in Fig. 4; distinction is made between DDT and its metabolites DDD and DDE. The results show clearly that concentrations in the canals, especially canal 4 (S. Francisco River, the main draining waterway for the agricultural area), reach values well above 100 ppb, concentrations which are comparable to those of the River Rhine and the River Elbe.

The depth profile for the Guanabara Bay core sample is given in Fig. 5; concentrations are based on sediment dry weight. It does not give information about the pollution history, because hydrological data, suggesting high stream

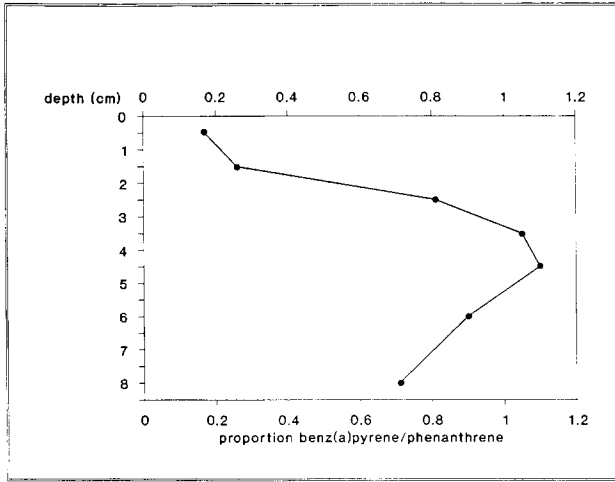


Fig. 6. Comparison between benzo[a]pyrene and phenanthrene concentration in the Guanabara Bay core sample.

velocities, as well as the physical structure of the core sample are not consistent with undisturbed sedimentation over a long period.

The depth profile shows concentration maxima at 1–3 cm depth for the chlorinated contaminants and a very significant concentration peak for PAHs at ~4 cm depth. The latter probably does not reflect a decrease in PAH input in recent years nor a high transport velocity through the sediment profile. It is likely that PAHs show more tendency than PCBs, DDT derivatives and Drins to adsorb to the small organic-rich particles existing predominantly at a depth of ~3–6 cm. Such differences in adsorption tendency can also be observed within the group of PAH congeners itself, differences which can be related to the polarity of the congener. Figure 6 gives the variation of the proportion benzo[a]pyrene/phenanthrene with depth. A non-polar PAH like benzo[a]pyrene shows more tendency to accumulate on the small-sized particle layer in the core than the more polar phenanthrene. The same results (but less clear) can be observed by comparing DDT derivatives and PCB congeners with different polarity.

Figure 7 shows the depth profile for the Guarapina Lagoon core; all concentrations are expressed on dry sediment weight basis. Here, the situation is quite different from the Guanabara Bay sample in that hydrological data as well as the physical structure of the core sample indicate a slow, undisturbed sedimentation in the lagoon. As shown in Fig. 7, organic carbon content is high (~10%) and constant down to 25 cm depth. Thus the profile may be used to obtain an estimation of the pollution history. Increasing PCB input (a factor of ~5) during the last 20 years and a less pronounced increase in chlorinated pesticide input can be observed from concentration variations throughout the depth profile. Clearly, this conclusion does not take into account biological degradation processes, which are usually not considered very important in the literature (see Brunner et al., 1985).

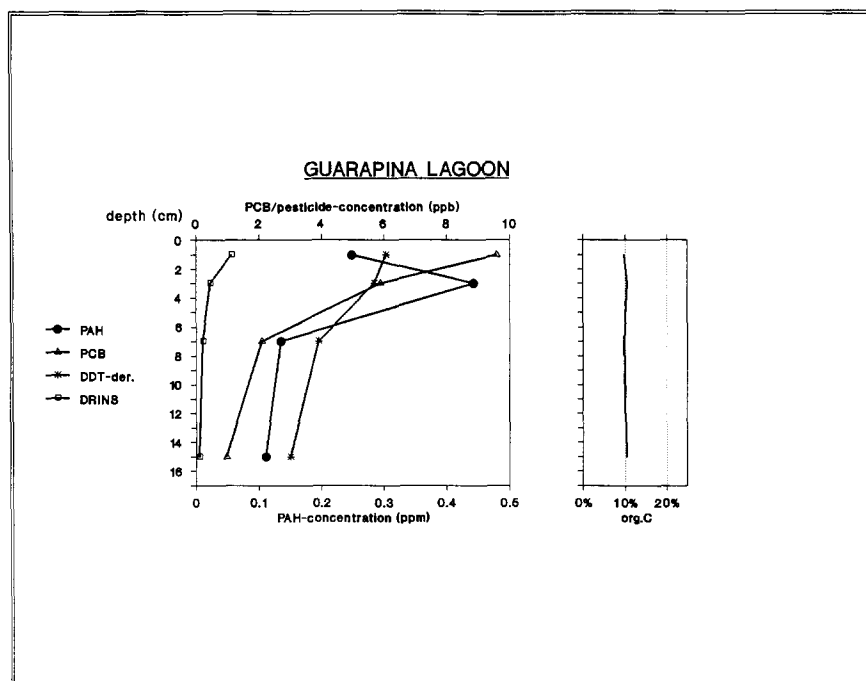


Fig. 7. Guarapina Lagoon core sample depth profile.

Figure 8 shows the depth profiles for the concentrations of DDT derivatives in core samples Sepetiba 1 and Sepetiba 2 (concentrations on dry weight basis). These two core samples exhibit quite different characteristics. The Sepetiba 1 sample contains high concentrations of DDT in the upper layer with the relative amount of DDD remaining constant throughout the depth profile. The Sepetiba 2 sample shows DDE predominating in the upper layer, low DDT concentrations, which remain constant throughout the depth profile, and DDD gradually disappearing with increasing depth. It is likely that the DDT and DDD degradation capacity of the sediment is quite different for the two samples.

The relatively high concentrations of non-metabolized DDT (compared with values obtained for European sea and river sediments) might be due to recent DDT inputs in the area or to less effective biological degradation in the tropical environment. The second hypothesis is more likely, because non-metabolized DDT is also found at increasing depth in the core samples, which is very rare in European coastal sediment samples.

CONCLUSIONS

At present, contamination of Rio de Janeiro coastal sediments with hydrophobic organic micropollutants of industrial origin (PAH, PCB) is not

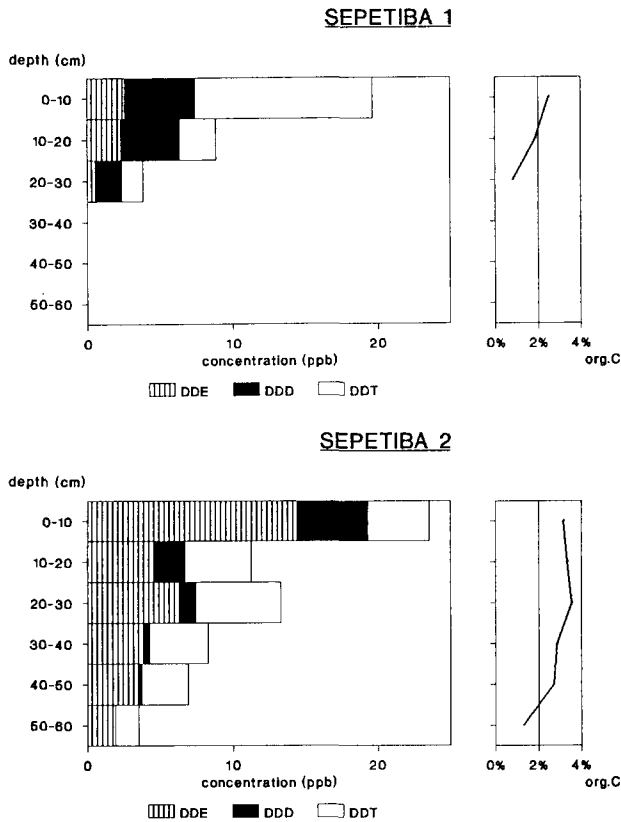


Fig. 8. DDT derivatives in two Sepetiba Bay core sample depth profiles.

alarming. A low-level pollution screening program with respect to these groups of contaminants in combination with input restrictions will probably be able to avoid problems in the future. On the other hand, contamination with persistent chlorinated pesticides is shown to be of more concern. A more extensive screening program, including more sampling sites and a larger group of pesticides, is advisable as a basis for future pollution control policy.

REFERENCES

- Brunner, W., F.H. Sutherland and D.D. Focht, 1985. Enhanced biodegradation of polychlorinated biphenyls in soil by analog enrichment and bacterial inoculation. *J. Environ. Qual.*, 14: 324 (and references cited herein).
- Japenga, J., W.J. Wagenaar, F. Smedes and W. Salomons, 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.
- Kuntz, K.W. and N.D. Warry, 1983. Chlorinated organic contaminants in water and suspended sediments in the lower Niagara river. *J. Great Lakes Res.*, 9: 241.

- Means, J.C., S.G. Wood, J.J. Hassett and W.L. Banwart, 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.*, 14: 1524.
- Onuska, F.I., A. Mudroch and K.A. Terry, 1983. Identification and determination of trace organic substances in sediment cores from the western basin of Lake Ontario. *J. Great Lakes Res.*, 9: 169.
- Patchineelam, S.R., C.M. Leitão Filho, K. Kritsotakis and H.J. Tobschall, 1988. Atmospheric lead deposition into Guarapina Lagoon, Rio de Janeiro State, Brazil. In: U. Seeliger, L.D. Lacerda and S.R. Patchineelam (Eds), *Heavy Metals in the Coastal Environment of Latin America*. Springer Verlag, Berlin, 1988, pp. 65–76.
- Wilken, R.D., I. Moreira and A. Rebello, 1986. Pb-210 and Cs-137 fluxes in a sediment core from Guanabara bay, Brazil. *Sci. Total Environ.*, 58: 195.