

Organotins in the sediments of the Zuari estuary, west coast of India

Sangeeta Jadhav*^a, Narayan B Bhosle^a, Paolo Massanisso^b, Roberto Morabito^b

^a*Marine Corrosion and Material research division, National Institute of Oceanography, Dona-Paula, 403004, India.*

^b*Environmental Chemistry Division, ENEA Casaccia, Via Anguillarese 301, 00060, Rome Italy.*

Abstract

Industrial use of organotins such as butyltins and phenyltins has increased several folds during the last two decades. Butyltins and phenyltins are synthetic, multipurpose chemicals, which have been extensively used in marine antifouling paints. They have been known to be extremely poisonous to mollusc fishery resources (oysters, clams, etc). Contamination of Zuari estuary sediments was assessed by quantitative determination of butyltins and phenyltins by using GC-MS using the electron ionization mode. Butyltins predominated in the whole area over phenyltins. Butyltins contributed about 70 –90 % of the organotins in general. The concentration of butyltins in sediments ranged from 20 to 7621 ng Sn/g. The concentration of phenyltins in sediments ranged from 0 to 46 ng Sn/g. Degradation indices for butyltins and phenyltins were calculated. The Butyltin degradation index (BDI) for the Zuari sediments ranged from 0 - 2.7 indicating a lot of fresh input of butyltins in the estuary and a lower degradation rate. The phenyltin degradation index (PhDI) ranged from 1-10 implying that different processes were prevalent at different stations. The observed organotin levels in the Zuari estuary indicate some highly localized areas of contamination which are severe enough to cause harmful effects on marine flora and fauna. Therefore, there is a need to regulate the use of butyltins and phenyltins as biocides in marine antifouling paints.

Keywords: Butyltins; Phenyltins; Degradation index; Sediments; Zuari estuary; west coast of India

*Corresponding Author. e-mail: sjadhav@nio.org; sangeeta.jadhav@gmail.com

1. Introduction

Organotin compounds such as tributyltin (TBT) and triphenyltin (TPhT) are toxic to many organisms. Due to this toxicity, they are widely incorporated in antifouling paints to control biofouling on industrially important structures. However, when released into water, organotin compounds are also often highly toxic to non-target organisms. For example, TBT at a few nanograms per liter can cause larval mortality, deformation of shells, and reduced reproduction in gastropods (Cheung et. al., 2003; Hoch, 2001). Therefore, it is essential to monitor the levels of organotin in areas subjected to shipping activities.

In India, organotin compounds are used as antifouling paints to control growth of fouling organisms on commercial and naval ships, and other industrial structures that use sea water. To the best of our knowledge, there is no legal ban on the use of TBT /TPhT based antifouling paints in India. Moreover, not much is known about the levels of organotins in marine waters, sediments and organisms collected from coastal environments of India (Rajendran et al., 2001; Bhosle et al., 2004, 2005).

The Zuari estuary is located on the west coast of India, and is used for ore transport, and navigation of small recreational ships and fishing boats from hinterland to Marmagoa harbour. Along the Zuari estuary, there are small jetties and wharfs that are used for berthing of small fishing vessels and barges. There are also some small workshops located on the banks of the river that are involved in repair, maintenance and construction of small ships and barges. River banks are covered with mangroves. Mangroves support several flora and fauna and serve as nursery grounds as well as nutrient sources to economically and ecologically important organisms such as prawn fishes and many other vertebrates. Therefore, the Zuari estuary is a sensitive ecosystem, and may be subjected to organotin contamination due to shipping activities. The main purpose of the present study was to evaluate organotin contamination in sediments of the Zuari estuary.

2. Materials and methods

2.1. Standards and reagents

Standard compounds monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT), triphenyltin (TPhT) and Tripropyltin (TPrT) were obtained from MERCK, Germany. All the compounds were of 97 - 98% purity. Pentyl

magnesium bromide (Grignard reagent) was freshly prepared in the laboratory, using Diethyl ether, Mg metal, Bromopentane and resublimed Iodine. These chemicals for the preparation of the Grignard reagent, and silica gel 40 were purchased from Sigma Chemical Co. All the other chemicals were of Analytical grade and were purchased from Qualigens, India.

2.2. Sampling

Sediment monitoring along the Zuari estuary was carried out in August 2006. Samples were collected from different locations to provide a representative coverage of Zuari estuary (Fig. 1). Surface sediments (0-5 cm) were collected with small van Veen grab and placed in portable icebox in aluminium foil and transported to the laboratory where they were frozen at -20 °C until analysis.

2.3. Sample preparation

Organotins were extracted from sediment samples following the method of Morabito et.al. (1995). Briefly, a sediment sample (1 – 2 g) was transferred to a clean test tube to which 15 ml of 0.03% tropolone in methanol, Tripropyltin chloride (TPrT) equivalent to 100 ng Sn (as internal standard) and 1ml concentrated hydrochloric acid were added. A blank was prepared by following the same procedure expect sediment. A standard mixture was prepared by adding 100µl of standard solution containing TBT (107 ng Sn), DBT (103 ng Sn), MBT (101 ng Sn), MPhT (106 ng Sn), DPhT (99.4 ng Sn), TPhT (102 ng Sn) and TPrT (105 ng Sn) to 15 ml. Of 0.03% tropolone in methanol. The samples, blank and standard were vortexed for 1 h to extract organotins. The supernatant was taken in a separating funnel and liquid-liquid partitioning is performed twice with 15 ml of dichloromethane. Dichloromethane extract was dried over anhydrous sodium sulphate. Iso-octane was then added as a keeper to avoid evaporative losses, extract was then evaporated almost to dryness, reacted with pentyl magnesium bromide (Grignard reagent). The derivatives were purified on activated Silica gel column. Concentrated to 1ml using gentle stream of Nitrogen and analysed by GC-MS as described below.

2.4. Instrumental analysis

A GC-MS system (Shimadzu QP 2010) equipped with a gas chromatograph and mass spectrometer detector with electron impact ionization mode (70 ev) was used for the analysis. The Organotins were separated and detected using RESTEK Rtx- 5MS capillary column (30 m, 0.32 mm i.d. 0.25 µm df) and selected ion monitoring (SIM) mode. Two microliters of sample or

blank or standard mixture were injected using a programmable on column injector. The injector was kept at 60 °C for 1 min then temperature was raised @100 °C min⁻¹ to 240 °C, and maintained at the same temperature for the rest of the run time. Initial column temperature was 80 °C. After 2 min the oven temperature was programmed to reach 280 °C at @ 10 °C min⁻¹. The interface temperature of the MS was maintained at 280 °C and ion source temperature was maintained at 250 °C. Helium was used as carrier gas (3 ml min⁻¹). The total run-time was 24 min. Data analysis was done by data processing software Shimadzu GC-MS solution Version 2.21.

2.5. Quantification, calibration and sensitivity

Quantification of organotins was performed by the internal standard procedure using TPrT as internal standard. Fresh standards were prepared to obtain calibration curves. Procedural blanks and standards were carried out for every set of 12 samples. To keep a check on the quality of analysis, a in house sediment reference material was analyzed with every alternate set of samples. Linear regression coefficient displayed a suitable linear correlation ($r^2 > 0.975$). The results obtained for the relative standard deviation (RSD) and percentage recovery are listed below (Table 1). These analyses showed adequate repeatability and precision for all the components. The minimum detection concentration for butyltins and phenyltins is 0.2 ng Sn/g.

3. Results and discussion

Surface sediment samples were collected from 9 locations in the Zuari estuary, west coast of India (Fig. 1). Sediments were analyzed for organotins to find out the levels of contamination due to these compounds. The concentration of TBT, DBT and MBT varied from 6.5 to 4353 ng Sn /g, 1.8 to 1030 ng Sn/g and 2.0 to 2238 ng Sn/g, respectively (Fig. 2 **a, b & c**). Similarly, the concentration of TPhT, DPhT and MPhT varied from ND to 16.8 ng Sn/g, ND to 16.8 ng Sn/g and ND to 12.5 ng Sn/g, respectively (Fig. 3 **a, b & c**). Phenyltins are relatively less abundant than the butyltins. Butyltins constitute about 70 to 90% of the total organotins. Spatial variations were clearly evident indicating localized areas of contamination. All the stations analyzed can be considered as contaminated with respect to TBT (i.e. TBT > 1.3 ng Sn /g) according to the classification scheme of Dowson et al. (1993). The highest concentration of both butyltin and phenyltin compounds was recorded at Sancole (SN). This station houses a small shipbuilding factory and dry dock unit. The concentrations are comparable to previous

data available from Marmagao harbour, Goa (Bhosle et al., 2004, 2005). Butyltins varied from 2.9 to 2027 ng Sn/g in the sediments of the Tuticorin harbour, east coast of India (Rajendran et al., 2001). The butyltin contamination levels recorded for the sediments of the Zuari estuary was found to be comparatively higher than that recorded for the Tuticorin harbour. Similarly, sediments collected from The Zuari estuary were highly contaminated with butyltins as compared to the sediments collected from Malaysia (18 to 1800 ng/g) and Gulf countries like Qatar, Bahrain and Oman (0.1 to 60 ng Sn/g) (Suderyanto et. al., 2004; Mora et al., 2003).

The presence of degradation products such as DBT, MBT, and DPhT and MPhT indicates biotic and/or microbial degradation of TBT and TPhT compounds, respectively. In order to predict whether the contamination is recent or not, butyltin degradation index (BDI) and phenyltin degradation index (PhDI) were calculated (e.g. Burton et al., 2005). BDI and PhDI were calculated according to the concentration ratios expressed in the following equations assuming similar degradation rates between both the compounds (Diez et al., 2002).

$$\text{BDI} = \frac{[\text{MBT}] + [\text{DBT}]}{[\text{TBT}]} \quad (1)$$

$$\text{PhDI} = \frac{[\text{MPhT}] + [\text{DPhT}]}{[\text{TPhT}]} \quad (2)$$

Where, MBT, DBT and TBT, and MPhT, DPhT and TPhT indicates concentrations of these compounds. Out of 9 sediment samples, 5 showed BDI values < 1 indicating fresh input of TBT and low degradation rate in the Zuari estuary. PhDI values ranged from 0 to 9.4 for the sediments of the Zuari estuary. For the stations DP, BM, RF and CR, the PhDI values are < 2 indicating moderate degradation of phenyltin compounds. Similarly, for the stations CD, BR, SN, JI and DP, PhDI values are > 2 implying rapid degradation of TPhT to DPhT and MPhT at these locations. The degradation products of organotins are far less toxic than the parent compound (Fent 1996). Degradation is therefore, a process by which remediation of contaminated sediments can occur involving natural attenuation processes (Burton et. al., 2004, 2006). The observed values of butyltins and phenyltins indicate that these sediments are contaminated with organotins and at some locations the contamination appears to be high enough to produce harmful effects on marine organisms.

4. Conclusions:

According to the classification scheme of Dowson et al., (1993), all the stations sampled in the Zuari estuary could be considered as contaminated (TBT > 1.3 ng Sn/g). Some of the stations of the Zuari estuary showed very high contamination of organotins. The high input of organotins particularly in sediments, overrides any removal by degradation pathway. To the best of our knowledge there are no sediment quality guidelines for organotins in India. TBT levels suggest that stringent legislative measures are needed to curb the usage of these contaminants in marine paints. Otherwise, organotins would have detrimental effect on our marine resources and ecosystem, which probably could not be reversed.

Acknowledgements

The authors thank Dr. Satish Shetye, the director, of the institute for support and encouragement. We are grateful to European Commission for financial support under project "Assessing the impacts of TBT on different coastal uses" (EC Contract No. PL 510658). We appreciate very much the help rendered by Mr. A. P. Selvam for the operation of the GC-MS system during the course of these studies. We are also thankful to Ms Anita Garg, Mr. Vishwas Khodse and Rammurthy Meena for their help during collection of samples. The first author thanks Mr. Michaele Fantini of ENEA, Italy for his precious help and support during her training at ENEA, Italy..

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Table 1
Relative standard deviation (n=5) and recoveries for organotins

| Compound | RSD (%) | Recovery (%) |
|----------|---------|--------------|
| MBT | 8 | 99 |
| DBT | 10 | 86 |
| TBT | 5 | 96 |
| MPhT | 10 | 80 |
| DPhT | 8 | 79 |
| TPhT | 12 | 94 |

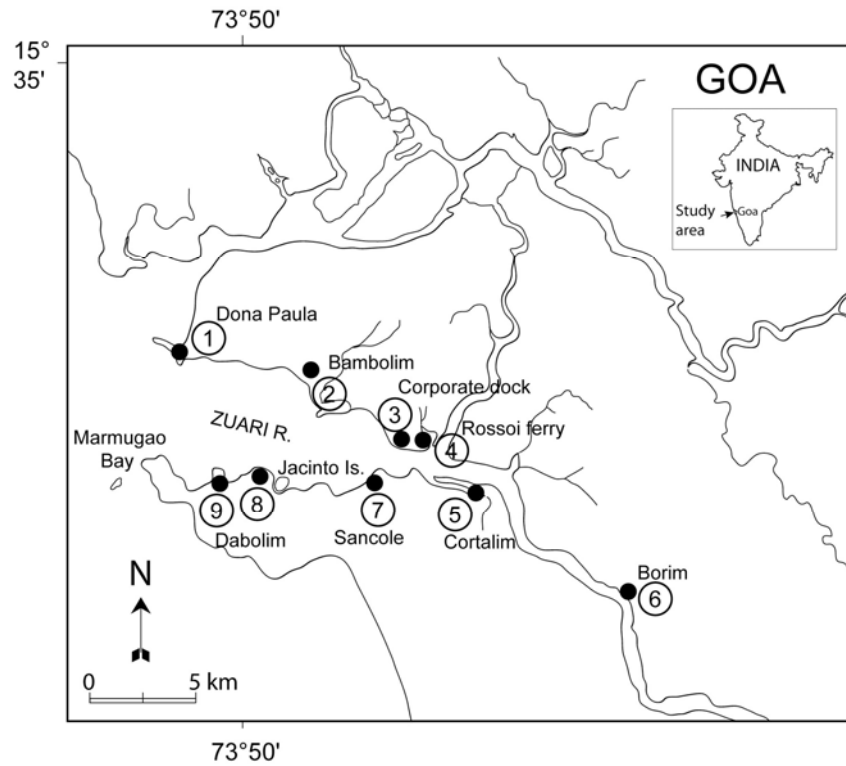


Fig. 1. Map showing the sediments sampling locations in the Zuari estuary, west coast of India

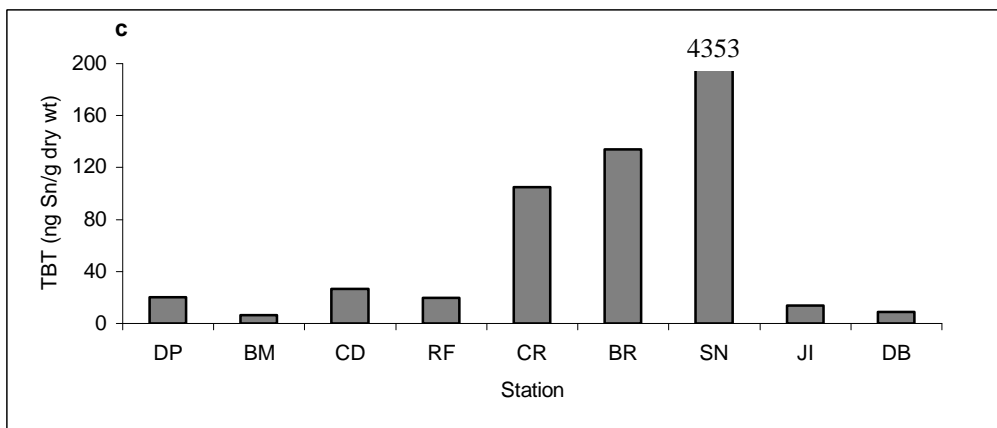
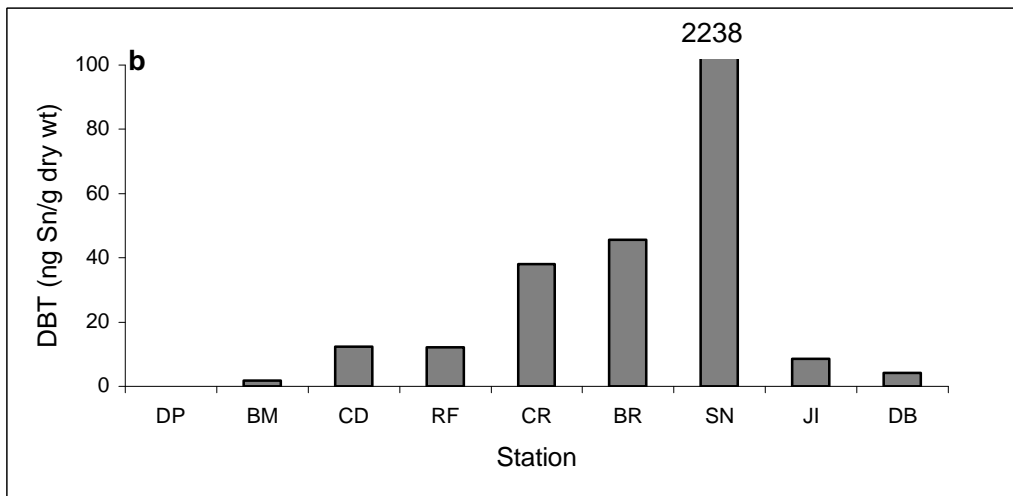
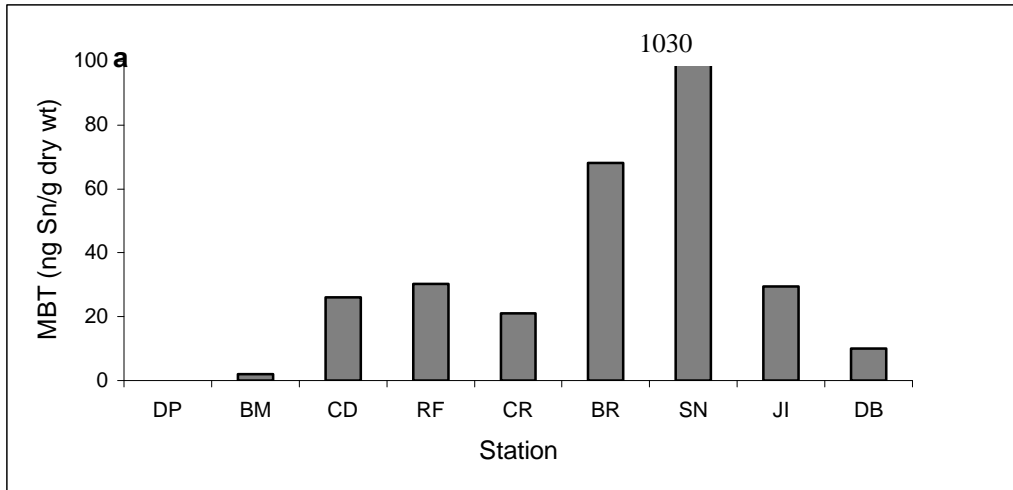


Fig. 2. Distribution of MBT (a), DBT (b) and TBT(c) at various stations in the Zuari estuary.
 (DP: Dona Paula, BM: Bambolim, CD: Corporate dock, RF: Rossoi Ferry, CR: Cortalim, BR: Borim, SN: Sancole, JI: St.Jacinto Island and DB: Dabolim)

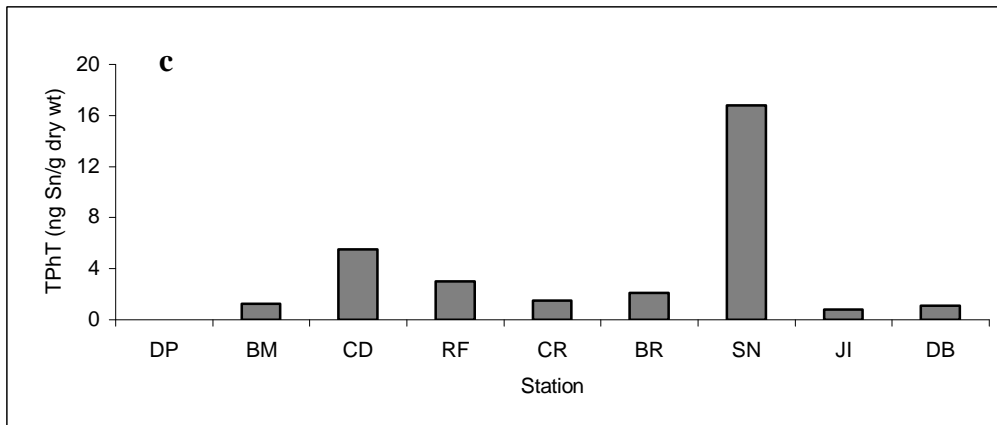
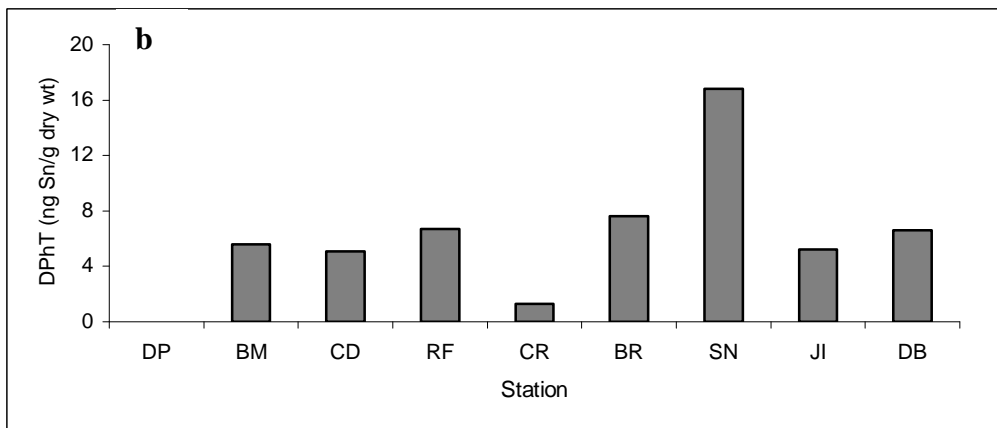
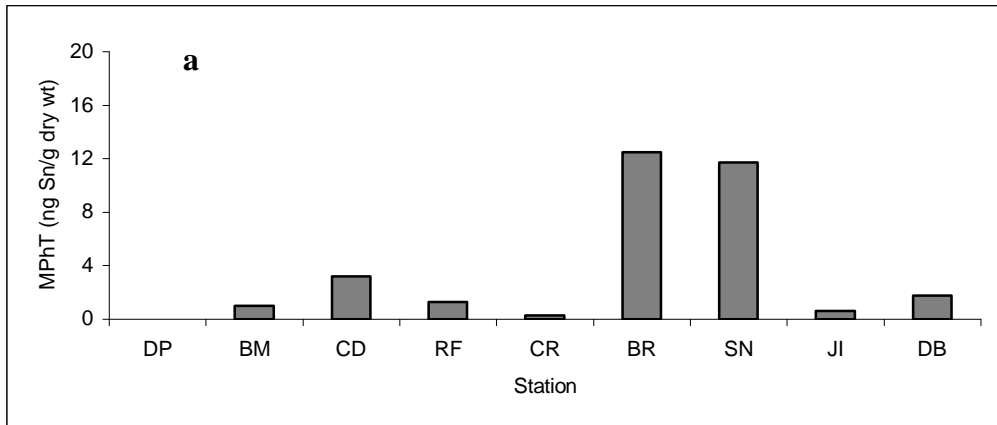


Fig. 3. Distribution of MPhT (a), DPhT (b) and TPhT (c) at various stations in the Zuari estuary. The station abbreviation as given in Fig. 2.

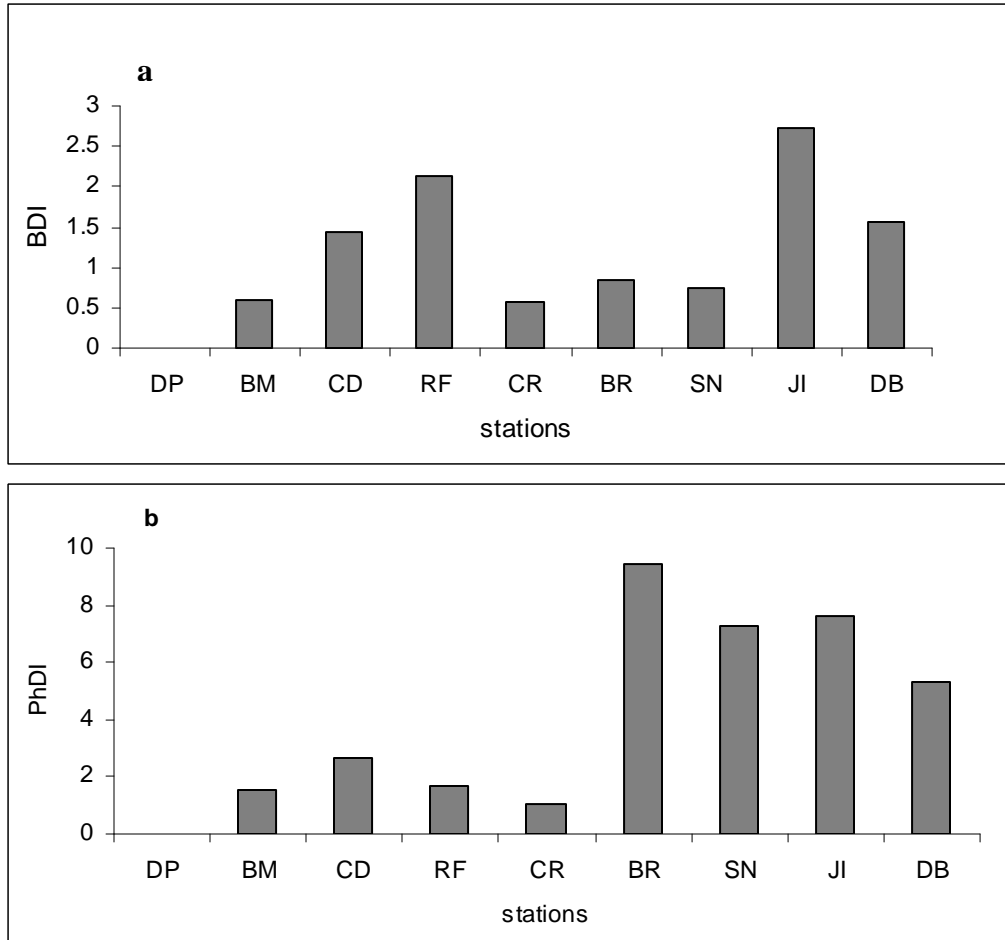


Fig 4. Butyltin degradation index (a) and phenyltin degradation index (b) for the Zuari sediments. The station abbreviation as given in Fig. 2.