NATURAL BIOACCUMULATING BROMINATED COMPOUNDS IN DOLPHINS AND WATERBIRDS FROM COASTAL AREAS OF TANZANIA

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame-retardants in polymer resins and plastics. By 2001 world market demand was estimated at 67400 metric tons. They are found in many home products such as furniture, TVs, computers, carpets and curtains. Contributing to about 30 % of the weight of the plastics. The chemicals are found as additive flame-retardants and not chemically bound to the matrix making them vulnerable to volatilization or detachment and therefore potential environmental contaminants.

Recent studies have indicate presence of brominated compounds in different matrices and they have been shown to be ubiquitous pollutant potential bioaccumulation ability in food web like PCBs. Most of these brominated diphenyl ethers (BDEs) are anthropogenic but some of them have been shown to be of natural origin. They are produced naturally in marine algae and sponges. The natural products include several congeners of methoxylated (MeO-PBDEs) and hydroxylated (OH – PBDEs) species Similar to anthropogenic BDEs, the natural BDEs are non-reactive, neutral and very hydrophobic compounds, indicating a pronounced enrichment in lipid-rich compartments and bioaccumulation in biota. However, their bioaccumulation mechanism from the primary producers (algae and sponges) is not clearly known.

Although little is known about their environmental and heath effects but their ubiquitous distribution, bioaccumulation ability and structurally similarity between MeO-BDEs and, e.g., PCBs and PCDD/Fs have attracted international attention. The possibility that natural MeO-BDEs have similar detrimental toxic effects and endocrine disruption properties as PBDEs and other known POPs is worrying.

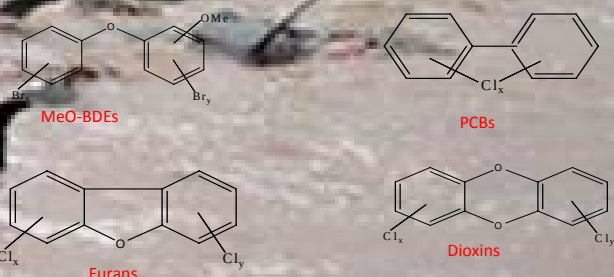

Figure 1. Structural similarity between natural BDEs and PCBs, furans & dioxins

OBJECTIVES

The concentrations and patterns of MeO-BDEs in blubber from *T. aduncus* and *S. longirostris* were analysed to assess:-
i) correlation between the compounds ii) Sex and age-related differences in accumulation of MeO-BDEs (maternal transfer) iii) Spatial variations

METHODOLOGY

This study involved analysis of blubber samples from two dolphin species; bottlenose dolphin (*Tursiops aduncus*) and spinner dolphin (*Stenella longirostris*) collected between 2000 and 2003 in the coastal waters of Zanzibar. A total of 8 - *T. aduncus* and 18 - *S. longirostris* blubber samples were analysed. The Samples were kindly provided by the marine mammals' project of WIOMSA.

Determination of Maturity

Dolphins were classified based on their reproductive condition as immature or mature. For female dolphins sexual maturity was determined from evidence of ovulation on either ovary, unless the female was obvious sexually mature at the time of capture (i.e., pregnant or lactating). Maturity classification for male dolphins was determined by histological analysis of the testes.

Extraction

The blubber samples were extracted by Solid Dispersion Extraction (SDE) method using cyclohexane solvent. The extract were concentrated to lipids using rotary evaporator and the obtained lipids samples were cleaned up using sulphuric acid treatment.

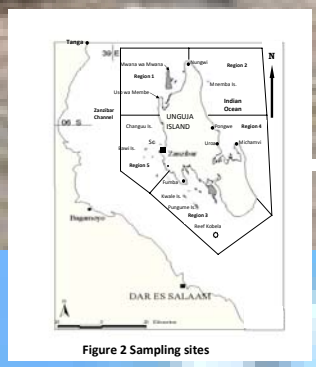

Figure 2 Sampling sites

Gas Chromatographic analysis

HP 6890 series GC equipped with two ECDs and two capillary columns of different polarity (SE-30 and OV-1701).

The identification of the MeO-BDEs was accomplished by comparisons of relative retention times (RRTs) of the compounds and RRTs of authentic reference standards on two GC columns with different polarity. Confirmation was done by the use of Gas Chromatography–Mass Spectroscopy (GC-MS). For GC-MS an Electron Capture Negative Ion (ECNI) full scan mode was employed to support the identification of the brominated compounds. The MS/ECNI spectra of the compound were compared with the spectra of authentic reference standards. Presence of MeO-BDEs was also possible by monitoring of the m/z 79 and m/z 81 fragment ions, characteristic fragment for MeO-BDEs m/z 159, 161 and 163 and for chlorinated species of the compounds m/z 114 to 119

The quantification was also achieved by comparison of peak heights of compounds and authentic reference standards in relation with internal standard peak height. Hexabromobenzene (HBB) was used as internal standard during the analysis.

RESULTS AND DISCUSSION

GC-MS/ECNI showed fragments m/z 79, 91, 159, 161 and 163 indicating presence of several brominated congeners. The spectra were dominated by low mass fragment ion of m/z 79 and m/z 91 while fragment of higher mass were found at relatively low intensity. Some of the spectra had fragments m/z 114, 115, 116 and 119, which indicated the presence of chlorine atomsin the compounds. However only two were compounds 6-MeO-BDE-47 and 2'-MeO-BDE-68 were quantified. The two compounds have been widely reported in different marine organisms elsewhere.

Ranges (median) concentration of MeO-BDE in ng/g lipid weight

Biota	2'-MeO-BDE-68	6-MeO-BDE-47
Spinner dolphin	1 200 - 150 000 (37 000)	1 800 - 140 000 (22 000)
Bottlenose dolphin	350 - 100 000 (11 000)	250 - 210 000 (13 000)

The overall mean concentrations of the ΣMeO-BDEs (6-MeO-BDE-47 + 2'-MeO-BDE-68) in spinner dolphins (77 000 ng/g lw) was more than five times the mean concentrations ΣOCs (HCB + DDTs + HCHs + cyclodienes) (13 400 ng/g lw) measured in the same samples. Similarly, the mean concentration of ΣMeO-BDEs in bottlenose dolphins (65 000 ng/g lw) was more than three times higher than the ΣOCs (20 000 ng/g lw) from the same samples.

Clearly, the naturally occurring brominated compounds can accumulate to concentration higher than the anthropogenic even in areas with relatively recent use of chlorinated pesticides.

Correlation between the measured Compounds

The concentrations of 2'-MeO-BDE 68 and 6-MeO-BDE 47 in both bottlenose and spinner dolphins were positively correlated (Figure 3) suggesting similar routes of exposure or mechanism of accumulation. The correlation was higher in bottlenose dolphins (R^2 =0.95) than spinner dolphins (R^2 = 0.87). Although transfer mechanism is still not clear as dolphins do not feed on algae, the higher concentrations of the MeO-BDEs reported in carnivores than in herbivore indicates that the accumulation is through the food chain

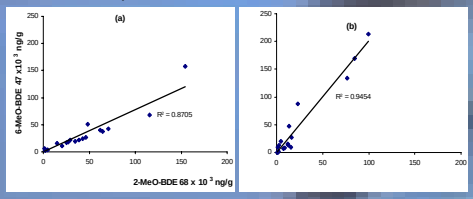

Figure 3 correlation of the quantified MeO-BDEs

Variation of the BDEs with Sex and Age

Variations of concentration with age differed between the sexes (figure 4). In males concentrations increase with age while in female concentrations decrease with age. It is likely that male dolphins accumulate MeO-BDEs throughout their life span resulting in an increase of pollutant loads with age and females accumulate the chemicals up to sexual maturity after which the concentrations decrease as the pollutants are passed to the offspring.

This phenomenon is called maternal transfer and can take place through placenta and lactation. Figure 5 confirms that MeO-BDEs are also maternally transferred (placental) concentration of 2'-MeO-BDE 68 and 6-MeO-BDE 47 in foetus are about 4% and 3% of the mother's burden.

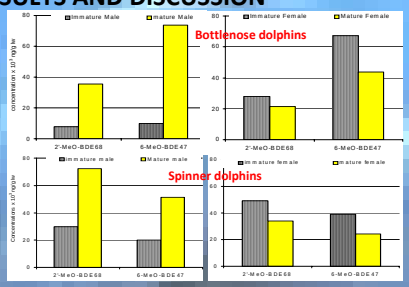

Figure 4 Variations of concentrations of MeO-BDEs with age and sexes

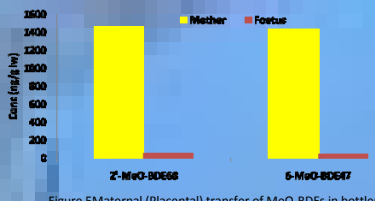

Figure 5Maternal (Placental) transfer of MeO-BDEs in bottlenose dolphin

Figure 6 Spartial variations of MeO-BDEs in dolphins

SPATIAL DISTRIBUTION

There was no general spatial trend of MeO-PBDE concentration between locations in the two species, however dolphins from Northern locations generally had higher levels.

Spatial concentration variations of MeO-BDEs

Spinner dolphin: 2'-MeO-BDE 68 : Mnemba > Nungwi > U. Membe > M. Mwana > Tanga
6-MeO-BDE 47: Mnemba > Nungwi > U. Membe >Tanga > M. Mwana

Bottlenose dolphin: 2'-MeO-BDE 68 : Nungwi >U. Membe > M. Mwana > Bagamoyo > Pungume > Changu > Tanga > Uroa
6-MeO-BDE 47 : Nungwi > U. Membe > M. Mwana > Bagamoyo > Changu> Pungume > Uroa > Tanga

Nungwi, U. Membe, M. Mwana and Mnemba sites are located in northern part of Zanzibar Island and therefore the findings indicate presence of potential of MeO-BDEs within the area. This calls for further investigations of the MeO-BDEs sources and their uptake as well as bioaccumulation mechanism in the area.

CONCLUSIONS

- Dolphins from coastal areas of Tanzania are contaminated with very high levels of various natural brominated compounds that are several times higher than anthropogenic POPs.
- The compounds seems to originate from similar routes of exposure and are maternally transferred to offspring.
- Maternal transfer of the compounds resulted to difference in trend levels with age between male and female
- The study shows spatial variations of residues which indicate presence of possible sources of the compounds in northern part of Zanzibar

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