Brazilian Experience on TBT Pollution: Lessons for Future Studies

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ABSTRACT


This work briefly reviews the findings on organotin pollution studies along the Brazilian coast. Several biomonitoring studies were made or are in progress, from N to S, including Pecém Harbor (CE), Mucuripe Harbor (CE), Natal Harbor (RN), Maceió Harbor (AL), Arraial do Cabo, Guanabara Bay, Ilha Grande Bay and Sepetiba Bay (RJ), and Santos Harbor (SP). Chemical studies were made in surface sediments of Guanabara Bay (RJ) and São Paulo and in biological samples of Guanabara Bay and Arraial do Cabo (RJ). Some bioassays on imposex induction were conducted for a native species, the marine neogastropod Stramonita haemastoma, including both laboratorial and field studies. Studies on the dispersion of organotin compounds from point sources were conducted at Arraial do Cabo and Ribeira Bay. Imposex occurrence is widespread along the Brazilian coast, being found in all studied areas. In areas closer to important organotin sources, sterility of females was frequently observed. Evaluation of imposex indexes showed lesser impacts in NE Brazil, due to a less intense shipping activity. Levels of organotin compounds like TBT (tribulyltin) and TPT (triphenyltin) found in sediment samples of Rio de Janeiro and São Paulo are similar to those found in polluted areas worldwide. Biological studies showed that both compounds are capable of imposex induction at environmentally realistic concentrations in a native species. The imposex response could also be used in the validation of numerical models. The importance of these findings for Brazil and other developing countries is discussed in the light of the global experience on marine antifoulings.

INTRODUCTION

Protection of vessels' hulls against fouling is a human need since ancient times, and nowadays antifouling protection is a business of billions of dollars. Much more recently, the role of fouled hulls in the transference of marine species have been also recognized as a global problem. As human populations in coastal areas grew, along with them also have grown cities, industries and the harbors and shipyards required for an always increasing marine trade. Now, multiple pressures on marine ecosystems are being felt in these areas, caused by the demands on natural resources and space that are frequently conflicting. The question of marine antifoulings is perhaps one the best examples of this kind of conflict. Organotin compounds, such as TBT (tribulyltin) and TPT (triphenyltin), have been used as biocides in antifouling paints on vessels' hulls since the early 1970s. Their efficiency in this role is a global consensus (CHAMP, 2000). In the other hand, these compounds showed to be persistent in the environment, to bioaccumulate and to be toxic to non-target-species (FINT, 1996; TEN-HALLERS TIABBES, 1997; HOCH, 2001). The use of these compounds is now controlled (restriction of use in boats smaller than 25m length was enforced in France, United Kingdom, USA, Germany, Canada, Sweden, Netherlands, Eire, Belgium, Austria, Norway, South Africa and Australia) or forbidden (Japan, New Zealand) in many countries (see CHAMP, 2000). These controls caused a general improvement in organotin pollution in these areas (e.g. REES et al., 2001), but near ports (e.g. MORGAN et al., 1998) or shipping lanes (RUZ et al., 1998, TEN HALLERS-TIABBES et al., 2003) there were still hot-spots of contamination even in controlled areas. The use of organotins as antifoulings is to be banned by IMO in a globally binding treaty by January, 2008 (www.imo.org). The convention, however, has not yet entered in force, and the ban is thus postponed.

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This work reports the findings of many studies on organotin pollution that were conducted in Brazil in the last years, and discusses these findings in respect to analytical methods, ecotoxicological research and legislative aspects. Location areas of these studies are shown in Figure 1, as well as the methodological approaches of each work.

Most of these studies used imposex development in Stramonita haemastoma as monitoring tool (1, 2, 5, 6, 7, 8) while in two others (3 and 4) Stramonita rustica was tested as bioindicator. The former species was tested with positive results for imposex induction by TBT and TPT in LIMAVERDE (2002), who followed the protocol proposed by HORIGUCHI et al, 1997 for Thais clavigera. Thus, Stramonita haemastoma could be considered a reliable indicator for organotin pollution. RIBEIRO (2002) transplanted organisms from a non impacted area to a highly impacted area of Arraial do Cabo (RJ), finding a positive result with the induction of imposex in females. A numerical dispersion model was tested in parallel, and the results were confirmed by the imposex monitoring and the bioassay (RIBEIRO, 2002). Until now, S. haemastoma is the only Brazilian native species tested for imposex induction, while many other species also showed imposex development.

Sterility was found in S. haemastoma (sites 3, 5, 6 and 7). In all situations, sterile females were found nearby important organotin sources, like Mucuripe harbor in Fortaleza (3), Forno harbor in Arraial do Cabo (5), inside Botafogo inlet, where Rio de Janeiro Yacht Club is situated in Guanabara Bay (6) and nearby Bracuhy and Frade marinas and Brasfels shipyard at Ilha Grande Bay (7). At least in one situation, Guanabara Bay, where the previous distribution of this species is known, a marked change occurred from the early 60's to the late 90's, and in two-thirds of the area once occupied by this species, populations are not found anymore. No sterility was recorded for S. rustica in Natal (3) and Maceió (4), but both harbors have much less ships/year than Mucuripe (2) and probably a much shorter water residence time than Forno harbor (5), a smaller harbor localized in a closed inlet. Shipping activities at sites 6, 7 and 8 are much higher and beyond any comparison. Anyway, actual water turnover times in these areas and the relative sensibility of these species are topics for further studies.

An interesting case study is Ilha Grande Bay area (7). Here, the most important organotin sources are small boats in
Key to the figure:
1) Pecém Harbor, CE (ongoing study, CASTRO et al.)
2) Fortaleza, CE (CASTRO et al., 2000)
3) Natal, RN (CASTRO et al., submitted)
4) Macaé, AL (CAMILLO JR. et al., submitted)
5) Arraial do Cabo, RJ (RIBEIRO, 2002)
6) Guanabara Bay, RJ (FERNANDEZ, 2001; FERNANDEZ et al., 2002; LIMAVERDE et al., 2001; LIMAVERDE, 2002, FERNANDEZ et al., submitted)
7) Ilha Grande Bay e Sepetiba Bay, RJ (PINHEIRO et al., submitted, this volume; ongoing study, QUADROS et al.)
8) Santos harbour, SP (STRUCHI et al., 1997)
9) Santos harbour, SP (GODOI et al., 2002)

Figure 1: Brazilian Studies on Organotins in October, 2003

Marinas, in the closest and shallowest inlets (see PINHEIRO et al., this volume) and big ships in a dockyard (Brasfels, ships over 300m length) and a big oil terminal from Petrobrás, the TEBIG (two berths for 200-300 000 ton. ships). These two point sources were located in a relatively open inlet, Japuíba, and in a rocky point nearby a deep channel, that separates Ilha Grande Island from the continent, reaching a depth of 50m. Even with greater organotin inputs estimated at Brasfels shipyard, the highest values of imposex indexes were found nearby the smaller marinas, showing that small boats are important sources of organotins in Brazilian waters and the effects of water residence time. The dilution of organotins by deeper waters and stronger circulation was observed both in the imposex indexes evaluated and in a 2D multiple-source dispersion model applied in this area. This latter observation confirmed also that biological data can be successfully used in the validation of this kind of model. Organotin speciation in surface sediments was studied in two areas: Guanabara Bay (6) and São Paulo state coast (9). In these studies, a similar analytical approach was employed. Organotins were extracted by sonication in a toluene-acetic acid 10:4 solution, using APDC (ammonium pyrrolidinedithiocarbamate) as a complexes agent, precipitation in a Grignard reaction and determination by GC/PFPD. Marinas accounted for the highest concentrations of TBT in Guanabara Bay (522 ng/g as Sn, DW, Botafogo Inlet) and in São Paulo Coast (Guarujá, 670 ng/g as Sn, DW). Santos harbor showed concentrations up to 360 ng/g, while the area near Ishikawajima shipyard in Guanabara Bay reached 422 ng/g. Low concentrations were found at Cananéia, SP, a small fishing area, 53 ng/g and much lower in the northern part of Guanabara bay, 10 ng/g, a protected area. The compound TPT was also detected (five out of nine sampling stations) in Guanabara Bay, in concentrations up to 39.9 ng/g as Sn DW, however it was not analysed in São Paulo. While measured concentrations are lower than other studies in tropical areas (max. 4500 ng/g TBT, Thailand, KAN-ATREKILAP et al., 1997) but similar to those found in another developing countries (max. 382 ng/g TBT, Korea, SHIN et al., 1999) or even of Arcachon Bay, a classical case.

While chemical methods for organotin analysis, as well as a suitable biomonitoring tool are currently available in Brazil, and also some local studies have already been made, there are still huge gaps in the current knowledge available for risk evaluation and risk assessment studies of these compounds. The previous question can be separated in three general classes:

**Analytical Methods**

Chemical analyses of biological samples or sediments are very expensive and time consuming, but are required for correct evaluation of environmental impacts. Fine, organic-rich sediments are the most important sink for organotins in coastal areas (LANGSTON and POPE, 1995) and could also be sources of these compounds to the water column (AXIAX et al., 2000). In the other hand, marine bivalves or gastropods are commonly used as food, and are the shortest way pollutants in the water can reach man. So, sediments and biological tissues analysis are priority in chemical methods development. Methods currently in use in Brazil have been successfully validated and may be improved to be easier and faster. Water samples, in the other hand, present lesser interferences than other environmental matrices, and are more suitable for simpler procedures. But the variability in the analyses concentrations caused by tides, currents, biological activities and the proper variability in shipping activities is great, leading to the necessity of a great number of samples analyzed before a consistent concentration level could be established at each area. No fast-and-simple water analysis protocol is in current use in Brazil for these compounds and this is an important research topic now.

Biological tools like imposex development could be useful if employed together with chemical monitoring in two ways: First, as screening tools, revealing the "hot-spots" for detailed studies on sediments or biota. This approach is probably the most economical for developing countries, and was successfully tested at Guanabara Bay, RJ (FERNANDEZ, 2001; FERNANDEZ et al., submitted). Second, imposex development could be used in the validation of numerical models for water circulation in impacted areas, as tested in Arraial do Cabo and Ilha Grande Bay (PINHEIRO et al., this volume). Once model is validated, predicted distribution pattern of organotins may be better chosen, and may also serve as new input data for the simulations.

**Ecotoxicological Research**

Risk assessment requires previous knowledge on both environmental fate and toxicity on native species for each compound or class of compounds. Today, basic ecotoxicological data on organotin effects on Brazilian native species are lacking, making risk evaluation an impossible task, and making also impossible the evaluation of damage already caused by organotins in our marine communities. Also, data on partition coefficients and half-lives of compounds in sediments and in water, which are required for predictive modelling, are missing. A strong emphasis should be given to these points, as these are the most important gaps in knowledge here, and legislative aspects depend on them. Bioassays with organotins could be used in the validation of numerical models for water circulation in impacted areas, as tested in Arraial do Cabo and Ilha Grande Bay (PINHEIRO et al., this volume). Once model is validated, predicted distribution pattern of organotins may be better chosen, and may also serve as new input data for the simulations.

**Legislative Aspects**

For seawater and estuarine waters quality parameters, the
basic legal reference in Brazil is the Resolution CONAMA 357 of 2005, which points to concentrations limits of 0, 10, 63 and 370 ng/L for preservation of species in natural reserves, mariculture in saltwaters, for protection of aquatic communities in estuarine waters and for navigation in saltwaters, respectively. While this is a considerable step forward, some of the proposed concentration limits are still high, however, and TPT was not considered.

Another problem arises from the question of the classification of the coastal water bodies, which depends on the drainage basins management committees, that in most cases are not working yet. It could take years before these limits could be properly applied. Concentrations levels as low as 2 to 7 ng/L TBT are capable of imposex induction in the gastropods Nucella lapillus or Buccinum undatum (Gibbs and Bryan, 1994; Davies et al., 1997; Mensink et al., 2002), while nominal levels of 100 ng/L TBT or 100 ng/L TPT are capable of spermatozoogenesis induction in ovary of female abalone, Haliotis gigantea (Horiguchi et al., in press). Reproductive impairment in the amphipod Caprella danielskii was found to occur at 10 to 100 ng/l TBT levels, and even the 10 ng/L level affects survival rates (Ojil et al., in press). A 48h EC50% value of 500 ng/L was found by Ruiz et al., 1995 for the brown Scrobicularia plana while levels of 310 ng/g can cause abnormal larval development and larval mortality in the marine polychaete Platynereis dumerilii (Hagger et al., 2002), so several taxa may be affected at the proposed levels. Another recent study by McAllister and Cline, 2003, showed that even levels as low as 0.1 ng/L TBT, presently below the detection limits in water, can cause a male biased population of zebrafish (Danio rerio) with a high proportion of sperm lacking flagella, if exposed to TBT for a long time period (70 days). These authors suggest that reproductive toxicity of TBT may be presently underestimated. As, even in protected areas, impacts of organotin pollution are being felt years after the establishment of local controls (Gibson and Wilson, 2003), this question will not be immediately resolved with the global ban, as well as the problem of the disposal of contaminated sediments (Champ, 2003).

CONCLUSIONS

Brazilian experience on TBT pollution was derived mostly of academical efforts. Today there's still no national policy on organotin compounds or the new antifoulings. This is a problem, as the data generated were not put together, and gaps on knowledge are not clear to the decision makers. They should act, even without total scientific knowledge, taking into account the precautionary principle derived from Rio and Johannesnburg Summits and the impacts verified. While some good chemical, biological and numerical tools have been tested in Brazil, much basic knowledge is still lacking to the problem of the disposal of contaminated sediments (Champ, 2003).

LITERATURE CITED


