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Predicted concentrations of biocides from antifouling paints in Visakhapatnam Harbour

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ABSTRACT

The concentrations of biocides leached from antifouling coatings are monitored in most of the developed countries. However, in India and many other developing countries, there is very little data available on the concentrations of biocides in ports and harbours. The first step was to obtain the order of magnitude levels of concentrations of biocides in the marine environment of the Visakhapatnam Harbour, and the MAM-PEC (Marine Antifoulant Model to Predict Environmental Concentrations) model was used to predict these values. The Visakhapatnam Port lies on the eastern coast of India, roughly halfway between Chennai and Kolkata, and is the largest port in India. This port is a natural harbour; the long and narrow outlet to the open sea makes it a 'poorly flushed' harbour. Predicted concentrations of tributyltin (TBT), copper, dichlofluanid, seanine, irgarol, diuron, tolylfluanid, and zinc pyrithione were computed. The results of the computations indicate that the levels of these biocides are comparable to those in many western countries. This gives credence to the fact that persistence of TBT and some other biocides is a global problem that cannot be ignored.

1. Introduction

Fouling on ship hulls has a deleterious effect on the performance of the vessel and, in a highly fouled vessel, it could account for up to 50% increase in fuel consumption. Biocide-based antifouling paints are widely applied on ship hulls to mitigate fouling. Since the 1970s, tributyltin (TBT)-based antifouling coatings became the industry standard, with over 70% of the vessels coated with such antifouling agents. However, the widespread use of TBT resulted in serious environmental problems and consequently, the use of these paints as antifouling coatings on ships hulls is currently banned. The paint industry has responded to this ban with a number of alternative antifouling formulations, which are primarily copper based. Copper alone, however, is not sufficient to prevent all forms of fouling and requires additional booster biocides for effective hull protection. Although copper and other booster biocides such as irgarol, diuron, dichlofluanid, seanine, tolylfluanid, and zinc pyrithione are considered safer than TBT, their chronic effect on the aquatic environment is yet to be determined.

Of all the biocides used in antifouling paint formulations, the persistence and the deleterious effects of TBT have been most widely documented (Alzieu et al., 1986; Bryan et al., 1986; Langston et al., 1997; Minchin and Minchin, 1997; Roepke et al., 2005; Stronkhorst et al., 1999; Swennen et al., 1997; Terlizzi et al., 2004; Yan and Yan, 2003). TBT is reported to be poisonous to a wide variety of organisms, including mammals (U'ren, 1983; Tanabe, 1988), and also enters the food chain of humans (Heidrich et al., 2001). In particular, TBT is known to interfere with the hormonal system of gastropods by disrupting their endocrinal system, which results in the masculization of the female species (Straw and Rittschof, 2004). The decline in commercial oyster production in Arcachon Bay, France, was attributed to the high levels of TBT (Alzieu, 1995, 2000). This led to the restrictions on the use of TBT by France and shortly afterwards, similar restrictions were imposed by the UK and USA (Champ, 2000). In the years that followed, many other countries began regulating the use of TBT. Since September 2007, the IMO led ban, which completely prohibits all forms of TBT-based antifouling paints on vessels, is in place. As a result of legislations restricting the use of TBT-based antifouling paints, some reduction in the levels of TBT has been reported – particularly in areas in proximity to recreational shipping (Rees et al., 2001; Hawkins et al., 2002; Jorundsdottir et al., 2005). However, in areas close to industrial shipping, the TBT levels are still high (Svavarsson et al., 2001; Fent, 2004; Santos et al., 2004). In USA, although there is a declining trend, TBT levels are still high around the ports (Valkirs et al., 2003; Venkatesan et al., 1998; Peachey, 2003). Very similar observations have been reported from Canada (Horiguchi et al., 2004), the UK (Harding et al., 1997; Morgan et al., 1998; Miller et al., 1999; Thomas et al., 2000, 2001; Galloway et al., 2004; Bray and Herbert, 1998; Harino et al., 2005), Spain, Portugal, Germany,

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Sweden, Poland, Italy (Gómez-Ariza et al., 2000; Diez et al., 2002, 2005; Hawkins et al., 2002; Birchenough et al., 2002; Minchin, 2003), Japan (Takeuchi et al., 2004; Murai et al., 2005; Ramaswamy and Tao, 2004; Harino et al., 2007), Australia and New Zealand (Gibson and Wilson, 2003; Burton et al., 2005; Smith, 1996) .

Monitoring of TBT in developing nations is very limited and, in most areas, the use of TBT is still not regulated. The use of TBT in antifouling paints is expected to continue in some Asian countries in years to come, primarily due to its relatively low cost and high effectiveness as an antifouling agent (Kwok and Leung, 2005). Of the data available in less-developed countries, there are reports of significant TBT concentrations along the Korean coastline (Shim et al., 2005). Mussels close to major harbours exhibited as much as 2500 ng/g dry weight of TBT. TBT concentrations as high as 560 ng/L have been reported in the coastal waters of Taiwan (Lee, 2001). Relatively low levels of TBT were observed in Indonesian coastal waters (Sudaryanto et al., 2004, 2005). No data, however, is available of TBT levels of areas in the proximity of major harbours. In contrast, higher TBT levels were observed in Malaysia, particularly in aqua-cultural areas (Sudaryanto et al., 2004), as compared to those in neighbouring Indonesia, where the monitoring of TBT is very sparse. Imposex was detected in gastropods in Phuket Island and the Gulf of Thailand (Swennen et al., 1997; Bech, 2002). In other coastal areas of Thailand, TBT concentrations in the range of 2–1246 ng/g of sediment were reported (Harino et al., 2006a). There are no reports of TBT levels in Vietnam, other than the fact that certain clam populations (*Meterix meterix*) have been affected by TBT (Midorikawa et al., 2004). Similar impacts have been observed in *M. meterix* and other seafood in China (Wang et al., 2005; Yang et al., 2006). In Hong Kong Harbour, TBT levels of the order of 500 ng/L were observed (Ko et al., 1995). Significant TBT levels were detected in a few areas in the Indian coastal waters (Rajendran et al., 2001) and concentrations of up to 2800 ng/g of TBT were detected in the sediment (Garg and Bhosle, 2005). However, as in other regions in Asia, extensive data on TBT concentration and its impact has not been reported in India. Comparatively low levels of TBT have been reported in the Gulf countries, despite heavy shipping traffic in the Arabian Gulf (de Mora et al., 2003). Sporadic data in TBT concentrations is available elsewhere in Africa and South America. The decline in the mussel species *Perna perna* in Algeria has been attributed to TBT pollution (Abada-Boudjema and Dauvin, 1995) and significant concentrations were observed in the Bizerte lagoon in Tunisia (Mzoughi et al., 2005). TBT concentrations of up to 2100 ng/g of sediment were detected in the Alexandria harbour (Barakat et al., 2001; Mohamed, 2005). Insignificant TBT pollution was observed in Ghanian ports of Tema and Takoradi (Nyarko and Evans, 1997). Variable TBT concentrations were observed at Durban and Richards Bay in South Africa (Marshall and Rajkumar, 2003). In Sao Paulo, Brazil, TBT concentrations as high as 670 ng/g in the sediment were reported (Godoi et al., 2003). TBT was detected in significant quantities along other areas in the Brazilian coastline, where conditions are very similar to that in India (Castro et al., 2005, 2007; Fernandez et al., 2005, 2006). Moderately high levels of TBT were observed in some areas in the Argentine coast (Penchaszadeh et al., 2001).

As with TBT, other biocides (such as irgarol, diuron, dichlofluanid, seanine, tolylfluanid, and zinc pyrithione) that are used in antifouling paints are also customarily monitored in most western countries, Japan, Australia and New Zealand (Liu et al., 1997; Voulvoulis et al., 2000; Thomas et al., 2001; Biselli et al., 2000; Okamura, 2002; Albanis et al., 2001, 2002; Martinez et al., 2001; Sakkas et al., 2002; Comber et al., 2002; Harino, 2004; Gardinali et al., 2004; Harino et al., 2005, 2007; Maxey, 2006; Carbery, 2006; Schiff et al., 2007; Srinivasan and Swain, 2007). In particular, irgarol

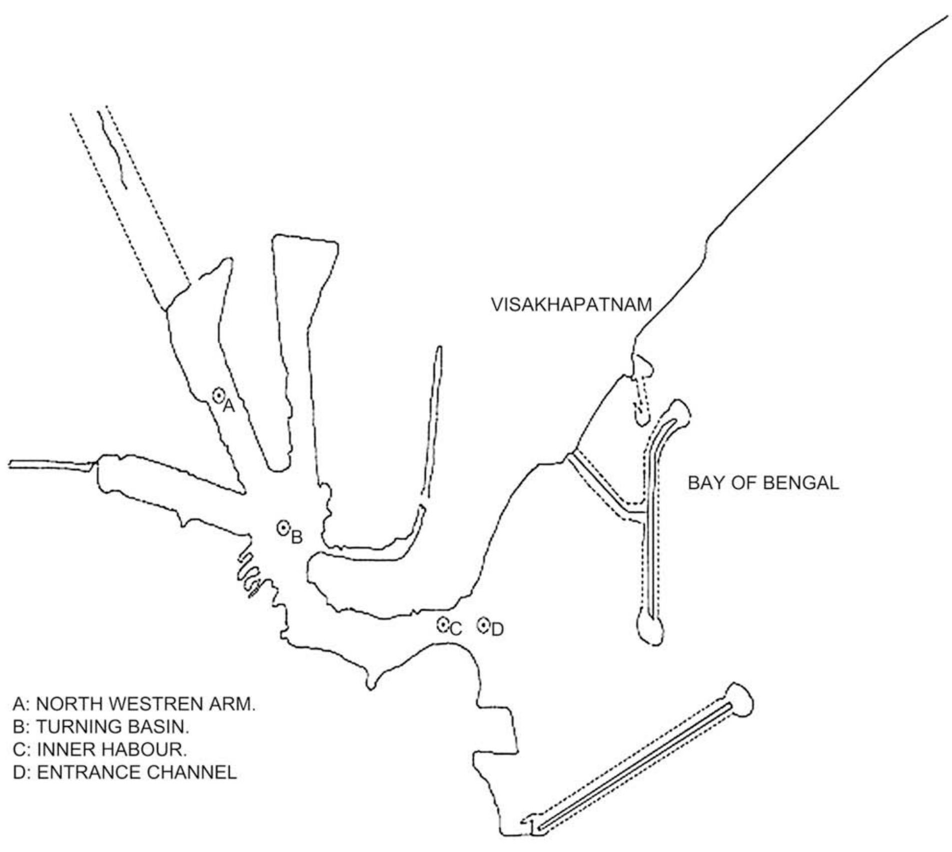

Fig. 1. 1Map of Visakhapatnam Port.