Environmental impact assessment of chemical protectants used in fishing industry

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Introduction

Any surface, immersed in seawater is subjected to the settlement of marine organisms (bacteria, algae, mollusks), known as fouling or biofouling. This unwanted colonization has serious impacts, in particular for the fishing industry, with deterioration of the surfaces, increased roughness, increased weight, increased fuel consumption, and loss of maneuverability of the vessels. Fouling growth can interfere with the operation of submerged equipment, impose increased loading stresses and accelerate corrosion on marine structures, and adversely affect the performance of ships by increasing hydrodynamic drag, which necessitates the use of more power and fuel to move the vessel through the water. Marine species may also be introduced into non-native environments through ship transport. Marine biofouling is a worldwide problem, costing billions of dollars per year in transportation.

The corrosion of vessels and structures immersed in the sea also pose significant economic and operational costs. The marine corrosion and biodegradation of materials can compromise the operation and structural integrity of vessels, structures and other immersed equipment. Control of fouling and corrosion would generate significant savings in both the maintenance and operational expenditure of maritime platforms and equipment. Biofouling has been and currently is globally important due to its environmental and significant economic impact; the estimated cost for transport delays, hull repair, cleaning and general maintenance is 150 billion USD per year (Schultz, 2007). Marine fouling can increase a ship's fuel consumption by 10–20%, besides, increasing sailing time with its attendant costs. Marine fouling on stationary structures adds mass and surface area, thereby increasing the force of wave action. Marine fouling inside pipes used by seaside power plants, roughens the surface (increases friction), reduces inside diameter, and increases the power requirements for pumping. In very severe cases, marine fouling can block completely the flow of water through pipes. Even microscopic fouling (bacterial films) can interfere with the effectiveness of power plants by reducing heat transfer through heat exchangers.

Antifouling (AF) coatings have been developed to prevent the settlement of fouling organisms. The earliest techniques proposed were pitch, tar, wax, heavy metals (lead), or toxic (arsenic-based) coatings. In the mid-1960s, self-polishing AF paints incorporating tributyl tin oxide (TBT-based compounds) were the first to show durable efficiency with a modest cost of production. TBT acts as a broad-spectrum biocide and can be incorporated into paints in such way that it is released from the coating and effectively inhibits fouling on a ship hull up to five years. However, in the late 1970s, the adverse effects of TBT became apparent. Several studies indicated that TBT-based compounds had adverse effects on aquatic life and more specifically on non-targeted fouling organisms such as bivalve molluscs, due to its high persistence and toxicity.

The impact of TBT on marine organisms urged many governments to restrict its use. France was the first country to ban the application of TBT-based AF paints on ships less than 25 m long in 1982. In October 2001, the International Maritime Organization took into account the adverse effects of TBT on the marine environment. An order was issued banning the use of this type of biocide in the manufacturing of AF paints from first January 2003 and the presence of these paints on ship surfaces from first January 2008. However, toxic coatings, especially regarding the tributyltin (TBT) era, were not without complications, of which we are now well aware. We are still using copper and to some extent, less favourable biocides on most ship hulls or other marine constructions.

The chemicals used in fishing technology for material protection is very disturbing to the sustainability of the marine ecosystem. The major disadvantages of use of chemicals are their instability, leaching, and high surface activity which lead to toxic reactions in marine organisms or environment. The restriction on the use of TBT led to a renewed use of copper-based paints and/or the use of new paints incorporating high levels of copper. However, copper (and other metals) may also pose problems for the environment. Copper based antifouling strategies were extensively employed as biocides in antifouling management by different workers due to its high efficiency against material degradation. But several researchers raised concern regarding the safety and toxicity of the copper based biocides. It has been well documented that maintenance of vessels painted with copper based biocidal coatings can also contaminate inshore environments (Schiff *et al*., 2004 and Turner *et al*., 2008). Study of Environmental Impact Assessment (EIA) system is vital to conform socio-economic development projects to environmental safety and thereby ensure sustainable economic development. It also helps the planning and management to take long-term measures for effective management as well as environment conservation.

Widely used Chemicals in fishing industry

Chemicals have very diverse applications and play an important role in the industry-dominated human society. Some chemicals are critically important for marine applications especially as anti-fouling, anti-corrosive and wood preservative agents.

Anti-corrosive chemicals and their mechanisms

There is a great demand for functional anti-corrosion coatings as a result of the tremendous degradation and losses to metallic structures due to corrosion. Chromium-based compounds and zinc have historically been the most common coating materials, but due to stringent health, safety, and environmental rules and regulations by many governmental agencies around the world, the usage of the former had declined progressively in the last two to three decades, while the application of zinc as a coating material is also significantly discouraged due to large price fluctuations. Self-healing anti-corrosion coatings can be a very beneficial alternative for the long-term protection of such structures. The term 'self- healing' is defined as self-recovery of the initial properties of the material after destructive action of the external environment. It should also be noted that the hindrance to the corrosion phenomenon by the protective coating is the most important criterion for calling the performance of the coating of self-healing as this automatically recovers the initial properties of the coating. There are many mechanisms by which anti-corrosion coatings operate, but generally these can be divided into three barriers:

barrier creation between substrate metallic materials and the surrounding environments; the inhibition of the corrosion process; and the coating acting as a sacrificial material.

Corrosion science involves the study of electrochemical processes taking place at electrodes. An electrode is essentially the boundary between a solid phase (i.e., metal) and a liquid phase (i.e., aqueous environment), and the corrosion processes take place across the phase boundary. The basic wet corrosion cell consists of four essential components: an anode, a cathode, an electrolyte, and connections. The first concept of corrosion control is that removal of any of these four components of the simple wet corrosion cell will naturally stop the corrosion reaction. From an engineering point of view, the major point of interest in corrosion science and engineering is the kinetics (or the rate) of corrosion reactions. The principal goal for studying corrosion reaction kinetics is to develop an empirical relationship that permits the prediction of corrosion rate under conditions that are different from those employed in the laboratory and to determine the mechanism of the overall corrosion process.

Anti-fouling chemicals

Antifouling coatings are used to prevent the settlement and growth of marine organisms on structures immersed in the ocean. The ocean is swarming with the planktonic forms of barnacles and other sessile marine organisms. Any object immersed in the ocean is rapidly colonized by a wide variety of organisms ranging from microscopic bacteria and algae to barnacles, tubeworms, bryozoa, oysters, and mussels. The accumulation of microscopic organisms is called microfouling while the accumulation of larger organisms is termed macrofouling. The settlement and growth of these organisms (collectively referred to as marine fouling) have significant adverse effects on structures in the marine environment. Copper-based antifouling coatings have been successfully used since the early days of wooden sailing ships when they were applied as sheets of pure copper metal or as overlapping copper nails. Modern copper-based antifouling coatings rely upon cuprous oxide as the principal toxic agent and contain up to 75 vol.% cuprous oxide.

Antifouling paints, that continuously release one or more biocides through the paint surface has been the primary method of fouling prevention on ships and other marine vessels for more than a century. However, by necessity, antifouling biocides are toxic, and can cause secondary environmental impact if the biocide does not quickly degrade after release and maintains its toxicity and bioavailability. Many antifouling biocides, such as mercury, arsenic, DDT and tri-organotin compounds, have been widely banned, and others, including copper, continue to be under scrutiny (Schiff *et al*., 2007).

Chemicals for wood preservation

Wood preservatives are substances applied to wood to protect it from degradation due to biological agents and different environmental conditions. Initially, natural wood preservatives like neem oil, sardine oil and cashew nut shell liquid were more prominently used. Later they were replaced with chemical preservatives. Over the past century, a variety of wood preservative methods including pressure treatment have been developed, that introduce a small amount of protective preservative into the wood cells (Edwin and Thomas, 2000). Preservatives that are widely used for pressure treatment of wood can be classified as oil borne, water borne (fixed and leachable) and solvent type. The water borne preservatives have largely replaced the oil borne preservatives like creosote for aquatic use, on environmental and human health considerations. Creosote was in use from 18^{th} century for the protection of railway sleepers. The water borne preservatives include chromated copper arsenate (CCA), chromated copper boron (CCB), ammoniacal copper arsenate (ACA), acid copper chromate (ACC), ammoniacal copper zinc arsenate (ACZA) and ammoniacal copper quat (ACQ). Solvent type preservatives include pentacholorophenol and copper naphthanate.

Chemical transformations in aquatic systems

Chemicals entering into an aquatic compartment from various sources, including from antifouling and anticorrosive paintings on boats will be exposed to a highly dynamic physical and chemical environment that leads to several transformations that will change their pristine physicochemical properties. Metals and metal compounds raise issues not generally encountered with organic chemicals. Metals are neither created nor destroyed by biological and chemical processes; rather they are transformed from one chemical species to another. These transformations, including dissolution, aggregation and sedimentation, are dependent on both physicochemical properties of the chemicals and those of the environment into which they were released. Metal elements and some inorganic metal compounds are not readily soluble and as a result toxicity tests based on soluble salts may overestimate the bioavailability and potential toxicity of these substances. Some metals are essential elements at low levels (e.g., copper, chromium, and zinc) but toxic at higher levels; while others which are non-essential (e.g., lead, arsenic, and mercury) bioaccumulate and are toxic. Many organisms have developed mechanisms to regulate accumulation of some metals to some extent, especially for essential metals. Each environmental form of the metal has its unique fate/transport, bioavailability, bioaccumulation, and toxicity characteristics (Zhang et al, 2018).

Environmental Impact Assessment of chemical contaminants (EIA)

Every anthropogenic activity has some impact on the environment. It is necessary to take up the activities for food, security, and other needs. There is a need to harmonize developmental activities with environmental concerns. Environmental impact assessment (EIA) is one of the tools available to planners to achieve this goal. It is desirable to ensure that the development options under consideration are sustainable. In doing so, environmental consequences must be characterized early in the project cycle and accounted for in the project design. The objective of EIA is to foresee the potential environmental problems that would arise out of a proposed development and address them in the project plan and designing stage. It integrates the environmental concerns in the developmental activities right at the time of initiating for preparing the feasibility report, which will enable the integration of environmental concerns and mitigation measures in project development. It can often prevent future liabilities or expensive alterations in project design. It is a policy and management tool for both planning and decision making. It assists in identifying, predicting, and evaluating the foreseeable environmental consequence of proposed development projects.

Objective of EIA:

The objectives of EIA are (i) to identify, predict and evaluate the economic, environmental and social impact of development activities (ii) to provide information on the environmental consequences for decision making and (iii) to promote environmentally sound and sustainable development through the identification of appropriate alternatives and mitigation measures.

The EIA is defined as: a policy and management tool for planning and decision making which assists to identify, predict, and evaluate the foreseeable environmental consequences of proposed developmental projects, plans, and policies. The outcome of an EIA study assists the decision maker and the general public to determine whether a project should be implemented or not. EIA does not make decisions, but it is essential for those who do.

Environment Impact Assessment Methodologies

The methods used to prepare and evaluate environmental impact assessment depend on the purpose and role of the assessment in determining public policy. While a rather simple and obvious connection must exist between purpose and methodology. It tends to highlight the fact that environmental impact assessment is used for a variety of purposes and therefore requires different methodological approaches. They are discussed below.

Leaching studies of chemical protectants

Leaching tests are frequently used to assess the potential risk of a waste to release organic and inorganic contaminants into the environment. Several leaching protocols have been developed with each differing in terms of leaching solution used, liquid-to-solid ratio, contact time, number of extractions and other testing parameters. The most commonly used leaching protocol is the US EPA Method 1311 for the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1992), which is designed to simulate leaching conditions in municipal solid waste landfills using a laboratory setup. For the evaluation on leaching of copper from the nano copper oxide treated polyethylene (PE) webbings can be assessed by modified ASTM D 1239 leaching method (Hingston et al, 2001).

Acute (Single-Dose) Toxicity Studies

Acute toxicity studies are conducted to evaluate the effects of a single substance. Usually each animal receives a single dose of the test substance in this study design. On rare occasion, repeated doses may be administered, but in any event, all doses are administered within 24 hours or less. Historically, a primary objective of acute toxicity testing was to determine an LD50 dose, or that dose which would be lethal to 50% of the animals treated (OCED 202, 2004).

Repeated and Chronic toxicity test

Chronic toxicity is defined as adverse effects occurring after the repeated or continuous administration of a test sample for a major part of the life span. Chronic toxicity occurs as a result of a repeated daily exposure to a chemical. The objective of a chronic toxicity study is to determine the effects of a substance following prolonged and repeated exposure. However, for this longer duration study, the number of animals per treatment group are larger to account for possible losses over the course of the study and to improve statistical power. Depending on the nature of the chemical, duration of exposure and the results in subacute/subchronic toxicity tests, chronic toxicity may be sufficiently addressed through a risk assessment (OCED 211, 1998).

Histopathological investigation

Histopathology is the study of the signs of the disease using microscopic examination of a biopsy or surgical specimen that is processed and fixed onto glass slides. To visualize different components of the tissue under a microscope, the sections are dyed with one or more stains. The aim of staining is to reveal cellular components and counter-stains are used to provide contrast. Hematoxylin-Eosin (H&E) staining has been used by pathologists for over a hundred years. Hematoxylin stains produce different colours in different organs, which make ease of identification of damage occurred in the cells (Fox, 2000).

Oxidative stress analysis using biomarkers

The biomarkers that can be used to assess oxidative stress have been attracting interest because the accurate assessment of such stress is necessary for investigation of various pathological conditions, as well as to evaluate the toxicity of chemicals. Assessment of the extent of oxidative stress using biomarkers is interesting from a physiological study. The markers found in blood, urine, and other tissues provide information of oxidative stress which can be assessed by antioxidant defence system (Burton, 2011).

Toxicity of chemicals used as an anticorrosive and biofouling compound

Toxic effects of various chemicals such as Nickel, Cerium, Copper, Silicon, Iron, Zinc, Arsenic, used for corrosive and fouling resistance were evaluated toward ecologically important species such as algae, molluscs, crustaceans and fishes. For all these species, it was found to be severely toxic since it affects their growth even at very low concentrations.

Effect on algae

Copper was found to be toxic for some algae. It can inhibit growth of *Chlorella vulgaris* and *Dunaliella tertiolecta*. Moreover, the photosynthetic activity can be blocked in *Chlorella pyrenoidosa* and visible lesions appear in macroalgae which was exposed to copper. Similarly, Irgarol shows highly significant toxicity in tests against several seaweeds. Also, the toxicity towards periphyton photosynthesis and for algal reproduction and for growth of *Selenastrum capricornutum* and *Enteromorpha.* (Alzieu, 2000).

Effect on invertebrates

Molluscs are moderately sensible to copper oxides when concentrations are less, whilst copper (II) chloride has no effect on the larvae of *Crasoostrea gigas* at the lower concentration during their embryonic development. Irgarol also showed the least toxic biocide on the embryonic development and the larval growth development of *Mytilus edulis* and *Perna lividus*.

However, CCA constituents, Cu was found to be more lethal to the clam of *Villorita cyprinoides* (Sreeja, 2008).

Effect on crustacea

Copper can kill the different crustacean species exposed more than 48 h. Larvae are more sensitive than adults. Investigation shows that the antifouling herbicide Irgarol 1051 lethally effects on larval and adult grass shrimp *Palaemonetes pugio*. Furthermore, Zinc pyrithione is toxic to juvenile *Elasmopus rapax* and toy shrimps *Heptacarpus futilirostris* even at low concentration. In many toxicology study of ZnPt on crustacean appears to be extremely toxic for the mysid shrimp and less toxic for *Daphnia magna* and *Tigriopus japonicas* (Alzieu, 2000).

Effect on fishes

Copper is lipophilic and shows only a slight tendency towards bioaccumulation. Exposure of copper reduces survival of Pagrus fish at a low concentration. Zinc pyrithione (ZnPT) is toxic to Japanese medaka fish *Oryzias latipes* and causes teratogenic effects, such as spinal cord deformities in embryos and on larvae of zebra fish *Brachydanio rerio* at very low concentration. Moreover, ZnPt is highly toxic to red sea bream *Pagrus major* since the secondary lamellae of the gill filaments of this fish were heavily damaged after exposure to this antifoulant (Mochida et al., 2006).

Environmental Legislation:

The first comprehensive environmental legislation (Section 102) in United States came into force on 1st January 1970 in the form of National Environmental Policy Act (NEPA). In India, the environmental impact assessment was started in 1976-77, when the Planning Commission asked the Department of Science and Technology to examine the river valley projects from environmental angle. This was subsequently extended to cover those projects, which required approval of the Public Investment Board. Then the Govt. of India enacted the Environment (Protection) Act on 23rd May 1986 to achieve the objective the decision that were taken is to make environmental impact assessment statutory. The Ministry of Environment and Forests issued a Notification on 27th January, 1994 making EIA statutory for 29 specified activities falling under sectors such as industries, mining, irrigation, power and transport etc. After following the legal procedure, a notification was issued on 27th Jan 94. 10th April, 1997 and 27th Jan 2000, making environmental impact assessment statutory for 30 development projects (Schedule I), the mandatory EIA clearance procedure started.

Current program implementation and research activities

Part of the implementation of EPA's water quality program is through the development of total maximum daily loads (TMDLs). A TMDL is the concentration of a chemical, or other pollutant, which can be added to a water body without causing the water body to exceed the concentrations needed to maintain its uses (e.g., swimming, fishing, drinking, aquatic life habitat, etc.). This concentration of the TMDL is then partitioned among all of the sources of the chemical to determine how much each source can discharge to the water body in question. TMDLs must be developed for all waters determined to be impaired. Metal is one of the principle reasons for water bodies in the US to be listed as having impaired water quality. Other contaminants in the top 10 include: mercury, pathogens, sediment, metals (not Hg), nutrients, oxygen depletion, pH, biological integrity, temperature, habitat alteration. The ranking specifically for metals (not Hg) puts copper, lead, selenium, and zinc in the top tier of water impairments due to metals (USEPA, 2006).

Conclusion

Considering the present situation, it can be assumed that with the further advancement of the fishing industry in India, particularly in systems undergoing intensification, the applications of chemicals would be increased. However, policy makers, researchers and scientists should work together in addressing the issues of chemicals used in fishing technology with the view to decrease the negative impacts. Therefore, both the government and non-government organizations should take initiative for better understanding of chemical uses in fishing technology.

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