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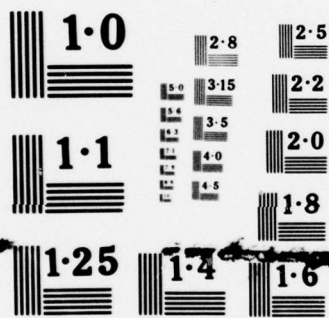
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REVIEW OF ANTIFOULING MARINE COATINGS AND THEIR INFLUENCE ON
MARINE ENVIRONMENTS

by

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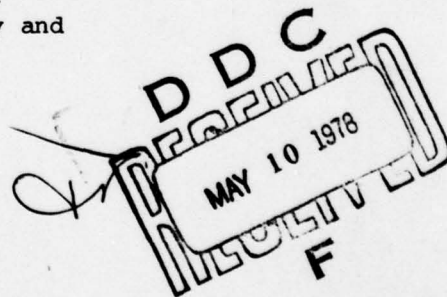
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ABSTRACT

The problem of marine "fouling" and corrosion of ship hulls and marine installations is well known and has been attacked by many research and development groups. The problem is particularly acute in south Louisiana where the brackish and salty water of the wetlands constitute one of the worse fouling areas in the world. The only practical solution to these fouling problems through the years has been the utilization of paints and coatings having antifoulant activity based on a toxic component. Currently, the most successful systems appear to be those containing organotin toxicants. As these materials find ever increasing utility and application in the marine industry and in naval operations, their long-term environmental impact on harbors and shipyards will become more important. The assessment of this environmental insult to the wetlands areas of south Louisiana is dependent on our ability to quantify the release of toxicant to the biosphere and to follow the biochemical pathway of the toxicant from release to eventual degradation as innocuous inorganic tin.

INTRODUCTION

In the warm waters of the world, marine "fouling" of ship hulls and marine installations is a well-known, but still unconquered, problem. In addition to the damage done to marine structures and ship hulls, the problem is compounded by the energy shortage. For example, "the drag caused by only a six-month accumulation of marine foulants can force a vessel to burn 40 percent more fuel just to maintain normal cruising

speed" (Starbird, 1973). The magnitude of the problem has been highlighted recently in the popular press (Starbird, 1974) and in general technology periodicals (Murray, 1975). Thus any program for fuel economy and marine installations preservation by the Navy, the shipping industry, or the fishing fleet must contain the development of effective antifoulant procedures as a high priority item. For marine operations in south Louisiana the problem becomes particularly acute since "Louisiana has a quarter of the nation's area in wetlands ranging from salty marine to brackish to nearly fresh water" (Frenzel, 1977). The marine and fishing industries are significant components of the State's economy and the fact that the Gulf Coast area is one of the worst fouling areas in the world makes the control of fouling organisms a "must" for this area.

The only practical solution to the fouling problem through the years has been the utilization of paints and coatings having antifoulant activity. Most of the coatings which have been developed are paint formulations containing a toxicant component. The most widely used toxicant has been cuprous oxide although various compounds of arsenic, mercury, lead and tin have been used. The cuprous oxide coatings are good fouling inhibitors but they have rather short effective life-times. The arsenic, mercury and lead coatings have been restricted in use or completely removed from the commercial market because of their possible toxicological problems, both in their preparation and application and in their inherent long-term danger in the environment. The tin containing coatings have been investigated by a number of groups, particularly by researchers at the Naval Ship Research and Development Center at Annapolis, Maryland. Studies have shown that tin antifoulants possess several advantages over conventional copper based coatings (Vizgirda, 1972 and Evans, 1970). For example, they provide superior antifouling over a longer period of time and when applied on conductive substrates, they do not promote corrosion. They exhibit control over several types of algae, marine borers and barnacles when properly formulated. Thus, the most promising antifoulant coatings which have been designed and characterized are those containing organotin toxicants. However, if these organotin containing coatings find widespread application in the marine industry and in naval operations, their long-term environmental impact on harbors and shipyards will become most important. It has been proposed that the organotin compounds degrade to non-toxic, non-cummulative inorganic forms of tin in the environment but there is no experimental evidence to support this proposition (Cremer, 1957; Sheldon, 1975; and Smith and Smith, 1975). Our own work in the characterization of the organotin containing coatings indicates that the toxicant materials are released to the environment as organotin hydroxides, thus indicating that their ultimate environmental fate and potential long-term hazards are unknown (Monaghan, et. al., 1977 and Good, et. al., 1978). The organotin moieties are known to be toxic to certain shellfish and other marine organisms as well as mammals, thus an evaluation of the environmental pathway associated with the organotin is essential to the continued and expanded use of these antifouling materials. Studies of the chemical and biological pathways of other toxic materials in the environment can act as a guide to what data must be collected and what experimental procedures must be carried out to define the role of organotin in the environment.

FOULING AND THE ENVIRONMENTAL FATE OF ANTIFOULING MATERIALS

Wood (Wood, 1974) classifies the elements of the Periodic Table into three categories depending on their toxicological behavior in the environment, (i) non-critical (ii) toxic and relatively accessible (iii) toxic but very insoluble or very rare. These are shown in Table -1. These toxic elements move through the environment under normal conditions by the "geocycle" (Figure 1) and become available to animals and plants. The metabolism of microorganisms plays an important role in mobilizing the toxic elements available in the environment. Microorganisms are capable of degrading the compounds either aerobically or anerobically or facultatively. They can also hydrolyze, hydrate and dehydrate or degrade the compounds available to them. Most of the very toxic elements become available to the microorganisms either from air pollution, water pollution, or from the soil. Our concern will be restricted to the environmental impact of antifouling materials which begin their geocycle as water pollutants. A number of review articles have provided critical evaluation of various antifouling materials used in marine coatings (Salve, 1950; Annon, 1952; Fisk, 1960). Alexander (Alexander, 1955) has judiciously reviewed the various advantages and disadvantages of these coatings and has classified them into four groups:

1. soluble matrix paints
2. permeable matrix paints
3. continous contact paints
4. exfoliating paints

The effective antifouling coatings must provide a steady toxicant leaching rate for a long period of time. Several investigators have determined the relationship between the leaching rate and the paint composition (Barnes, 1947, 1948 and 1951) and the leaching rate and the pigment particle size (Alexander, et al, 1951). The antifouling properties of the organotin containing coatings have been investigated and these studies have shown the advantage of the organotin toxicants over the conventional copper antifoulants (Bennett, et al, 1966; Evans, 1971; Corksley, et al, 1966). The organotin coatings provide superior fouling control with less toxicant over a longer period of time. However, extensive leach rate data and specific knowledge of the toxicant release mechanism are not yet available for the organotin systems.

If we are to avoid problems such as those confronting residents in the Chesapeake Bay area (Hirzel, 1978), immediate attention must be given to the pollutants distributed to the Louisiana wetlands by various activities of man. The toxicants from antifouling coatings are only one source of such pollutants but the potential usage (estimated at 24 million pounds annually in the United States) and known toxicity of the organotin systems make them crucial materials for study. Their biochemical transformation and transportation in the environment must be determined so that efforts to minimize their environmental impact can be optimized. To do so it will be necessary to chemically follow them from their input into the environment, determine their possible uptake in the food chain, and evaluate their ultimate effects on the entire ecosystem. The input mechanism is not only leaching from ship hulls but also from shipyards and harbors where hulls are re-coated and from plants manufacturing the coating materials. Our own work at the University of New Orleans has been focussed on the development of experimental techniques for chemically characterizing the tin species actually in the coatings and those released

TABLE - 1

Noncritical			Very toxic and relatively accessible			Toxic but very insoluble or very rare	
Na	C	F*	Be	As	Au	Ti	Ga
K	P	Li	Co	Se	Hg	Hf	La+
Mg	Fe	Rb	Ni	Te	Te	Zr	Os
Ca	S	Sr	Cu	Pd	Pb	W	Rh
H	Cl	Al	Zn	Ag	Sb	Nb	Ir
O	Br	Si	Sn	Cd	Bi	Ta	Ru
N				Pt		Re	Ba

* Some may argue with this designation, but we do add fluoride to drinking water. + All the lanthanides are very insoluble and some are very rare. (From Wood, 1974).

to the environment. To improve the efficiency of the coatings and to minimize the environmental impact of the materials we need to also understand the fouling mechanisms (how the fouling organisms grow and attach to marine structures), the "killing" mechanisms (how the toxicant affects the fouling organisms), and the leaching mechanism (the amount and species of organotin released to the environment).

Fouling Mechanism

A number of factors influence the attachment of fouling organisms to the surface of the paint coatings (de la Court, et. al., 1973):

1. geographical and seasonal influences
2. movement of water
3. texture of the surface
4. light and illumination

The fouling organisms can be illustrated by the barnacles and algae.

Barnacles are small sea animals with a shell which attach themselves to ship-bottoms or submerged surfaces. The two most common species are the acorn barnacle and the goose or ship barnacle, characterized by a stalk (peduncle) which supports the body and serves as an organ of attachment. Barnacles are arthropods; marine crustaceans having feathery appendages for gathering food. Both free living and communal forms are found. Many species inhabit the intertidal zone, others are found below the low tide mark, and still others remain at considerable depth. Most of these barnacles are hermaphroditic and must settle close to each other in order to facilitate cross-fertilization. The fertilization and development of zygotes occur in the mantle cavity of the parent and the microscopic larvae (nauplias larvae) escape from the eggs and become

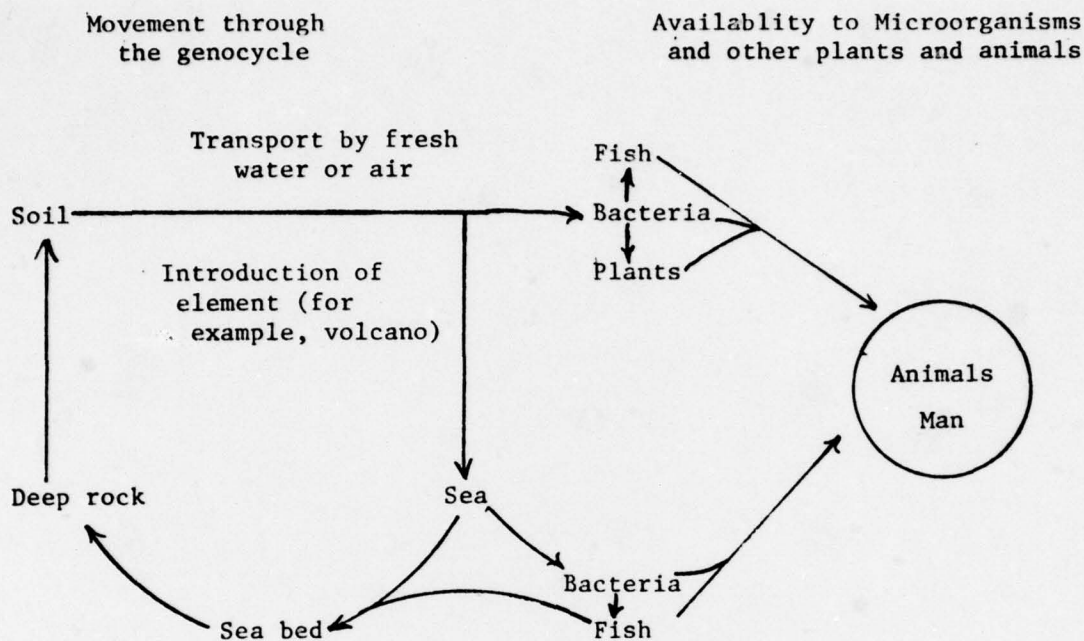


Figure 1: The movement of toxic elements through the geocycle and their availability to microorganisms and other plants and animals. (From Wood, 1974).

free swimming. After a week or so they transform into cypris larvae; bivalved larvae which attach initially to the substratum using suction cups, followed later by the secretion of cement. This cement is formed in a pair of glands found near the compound eyes of the cypris. Later on the bivalve shell is lost and a complete change in the body occurs as the sessile (directly attached) adult stage is reached. Saroyan and coworkers (Saroyan et. al., 1969) have reported that the cements secreted by the cypris and the young adult barnacles have the same composition and contain nearly 80 percent protein. The exact composition of this cement has been the subject of a number of studies, but no definitive delineation of its properties and hardening mechanism has been made.

The settling and metamorphosis of the barnacles are influenced by the presence of an antifouling coating. It has been postulated that the toxicants in the coatings poison the cypris and young barnacles, preventing their settling. Coatings having high leaching rates are presumed to kill the cypris larvae well before they complete their metamorphosis, while the coatings exhibiting low leaching rates are expected to slow down the metamorphosis and disrupt the barnacle life cycle. Long exposure to low toxic action therefore retards the accumulation of barnacle buildup on substrates.

Algae constitute a very different type of marine fouling. These sea plants can reproduce asexually viz. fragmentation, cell division etc. Marine algae reproduce by an alternate cycle of sexual and asexual means; i.e. by means of gametes and zoospores. Christie and Evans (Christie, et. al., 1962) have shown that the liberation of gametes and zoospores by Thalli depends upon external conditions such as the strength of the tide, light and temperature. Zoospores remain mobile for about a week so that they can settle on a surface. Immediately after settling these organisms secrete an adhesive material which attaches them to the substrate. After initial attachment, it takes a few hours for the algae to settle firmly on the surface and to resist being washed off. The prevention of fouling by algae has been accomplished by the use of enzymes, plant hormones, and antifouling chemical toxicants. Unfortunately, the algae spores can easily survive on the surface of an aged antifouling coating where they concentrate at the spots which have low toxicant concentration. Thus it is difficult to prevent algae fouling for long periods of time.

Toxicant Leaching from Coating Surfaces

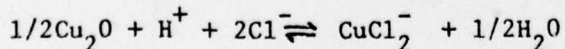
The leaching mechanisms for the antifouling toxicant and the speciation of the chemical form of the released toxicant have been the subject of extensive research. Models to depict the leaching process have been designed for various types of coatings. These models are important to an eventual understanding of the antifouling process and the design of antifouling coatings which are both effective and offer minimal insult to the environment. Several of these leaching models are outlined below to give the reader an appreciation of the current "state-of-the-art" in our understanding of antifouling coatings and their mode of action.

1. Toxicant Release from Intact Binders - A number of models have been advanced to describe the leaching mechanism in continuous contact coatings (Ketchum, et.al. 1945, 1946; Ferry, et. al., 1946; Marson, 1964, 1969, 1974). Vinyl and chlorinated rubbers or rubber resins are commonly used as binders in these materials. The coating is assumed to consist of a porous skeleton (provided by the binding material) which supports the toxicant and acts as a porous membrane during the leaching process. The models have been developed primarily for coatings containing cuprous oxide as a toxicant. The observed leaching rates decrease with time (aging) and the toxicant concentration required for effective contact antifouling properties is less than that required for the detection of leached toxicant in the surroundings. To explain these observations, Ferry and Ketchum, (Ferry, et. a., 1946) have proposed that direct contact is required between toxicant molecules. Assuming hexagonal close packing of the toxicant in an idealized coating, as the toxicant concentration is reduced through leaching, the number of toxicant molecules in close contact decreases, resulting in a corresponding decrease in the leaching rate. Thus the total amount of soluble toxicant in the coating determines the leaching rate. This explanation accounts for the fact that effective copper oxide containing coatings lose their effectiveness over a relatively short period of time depending on the

relative concentration of toxicant, thus requiring high levels of toxicant loading for successful coatings.

Marson (Marson, 1969) has proposed a theoretical model for idealized continuous contact paint films and has developed a mathematical equation for the leaching rate. His model is based on the following assumptions: (1) In an idealized paint film, the pigment (toxicant) particles are spherical and of equal size; (2) The binder is inert and insoluble; and (3) The thin film of the binder which separates the toxicant particle is brittle and undergoes fracture due to the osmotic pressure differential. When the film is immersed in sea water the toxicant particles at the surface dissolve forming a saturated solution at the coating - leachate interface. As the diffusion of the solvated particle proceeds, the thin film of the binder is uncovered, the solvent diffuses through the coating, and the toxicant is dissolved. The resulting osmotic pressure ruptures the film with the size of the hole formed dependent on the strength of the binder and the osmotic pressure. The dissolved toxicant must diffuse through the interconnecting holes and the smaller the holes, the greater the reduction in leaching rate with time. All of these factors have been combined and Marson (Marson, 1964, 1969, 1974) has applied the basic Stokes-Einstein diffusion equation to the idealized systems with some success. The limitations of the Marson model are: (1) The leaching concept developed for idealized systems is not achieved in reality; and (2) The fracturing of the paint film due to the difference in osmotic pressure is doubtful in that high osmotic pressures occurring in salt solutions may cause blisters in the coating surface rather than brittle fractures.

de la Court and de Vries (de la Court, et. al. 1973) have modified the diffusion model and determined the relationship between the leaching rate and a number of experimental variables, such as matrix thickness, flowrate, chloride and copper concentrations, temperature, and coating composition. Their model is simple and differs from Marson's model in that no assumptions are made regarding the shape and distribution of the toxicant particles in the coating film. The resulting leaching mechanism is pictorially presented in Figure 2. If the coating is on a ship hull moving at relatively high velocities, the coating thickness decreases and the flow in the boundary layer changes from laminar to turbulent. The copper oxide dissolves in the sea water to establish a reaction equilibrium as follows:



The following processes take place during the actual leaching: (1) The diffusion of Cl^- and H^+ ions from the boundary layer to the paint surface; (2) The diffusion of these same ions through the leached matrix to the unleached matrix; and (3) The dissolution of the copper oxide; the diffusion of the copper chloride complex to the coating surface (through the leached matrix), through the boundary layer into the bulk of the seawater. It is assumed that processes (2) and (3) are slow and constitute the rate determining steps. The concentration of CuCl_2^- must be built up at the interface between the leached and unleached layers; the ions must then diffuse to the surface of the coating. Under stationary

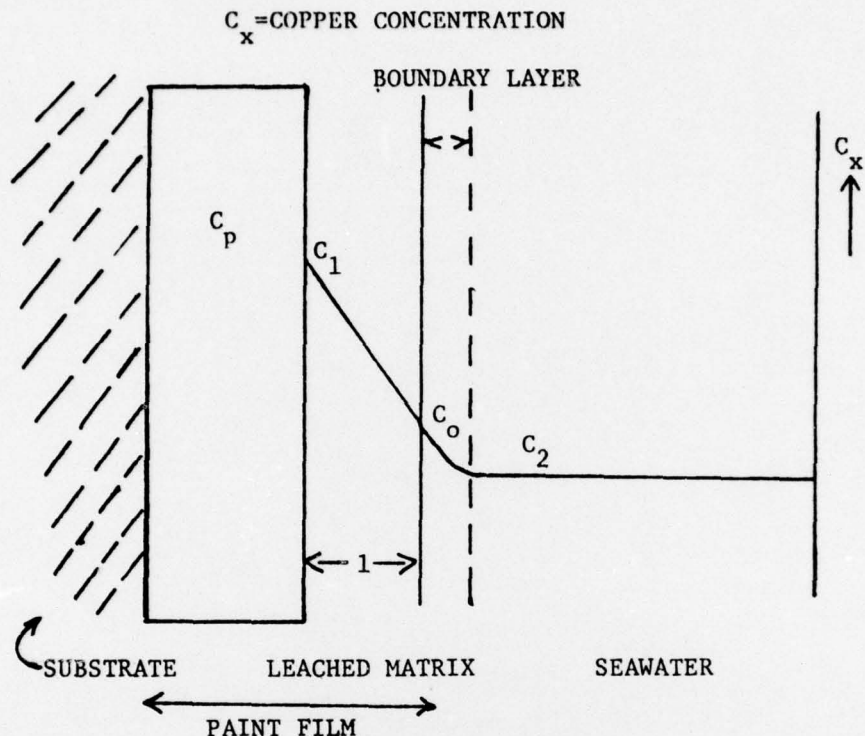


Figure 2: Cross-section of a leached paint film. C refers to copper concentration (from de la Court, et. al. 1973).

conditions (where a ship is moored in a harbor), the leaching rate remains the same in both layers and the diffusion equation for defining the leaching rate can be modified accordingly.

Continuous contact coatings containing copper oxide are more effective if the toxicant is uniformly dispersed in the paint film as finely divided particles. It has been empirically determined that the distribution of young barnacles in an aged antifouling coating is not uniform, the barnacles are concentrated at spots having the lowest toxicant concentration. An example of a continuous contact antifouling coating is the American Naval specification 121, MIL-P-15931A of the following composition:

Copper oxide	46.5% (by weight)
Vinyl resin VYHH	19.8%
Rosin WW	25.2%
Tricresyl phosphate	8.5%

The copper oxide can be replaced by strontium chromate without diminishing the antifouling properties of the coating.

2. Toxic Release from Soluble Binders - Coatings in which the

toxicant is dissolved simultaneously with the binder are referred to as soluble matrix paints. These materials can contain relatively low percentages of toxic material and still remain effective. The leaching rate in these materials is dependent to a large extent on the nature and amount of extender used in the coating. Coatings containing soluble extenders have higher leaching rates than those containing equivalent amounts of non-soluble or low solubility extenders (Partington, et. al. 1962). Coating manufacturers can thus optimize the effectiveness of their materials by choosing total systems having suitable components for the paint characteristics desired. The soluble matrix paints generally have shorter antifouling action than the continuous contact paints and are therefore less popular. An example of a soluble matrix coating is represented by the following formulation (de la Court, et. al. 1973):

Formula 15RC coal tar rosin

Component	parts by weight
Zinc Oxide	238
Silica	78
Magnesium silicate	72
Cuprous oxide	145
Mercuric oxide	45
Rosin WW	248
Coal tar naphtha	47
Coal tar	6.4
Pine oil	5.2

Coatings of the above type which contain wax are solids at room temperature but they soften at about 60°C. These coatings are generally applied at 140 - 150°C. Since paraffin wax is biodegradable, it provides a poorer antifouling material than those containing microcrystalline waxes. In general, materials of this type are difficult to apply and difficult to remove when their antifouling capacity has been exhausted.

3. Coatings Containing Organometallic Toxicants - During the last decade a variety of antifouling coatings have been designed using organometallic compounds as toxicants. Organoarsenics and organomercurials show excellent antifouling activity but their use has been restricted for toxicological reasons. The biological cycle for mercury (Figure 3) and the biological cycle for arsenic (figure 4) have been delineated. The long-term environmental insult of these materials is thought to be serious because of their introduction into the food chain as seen in Figures.

As early as 1943 it was noted that triethyl and triphenyl tin exhibited antifouling activity (Cooksley, et. al. 1966). However, the organotins were not exploited until 1954 when the work of Van der Kerk and Luijten was reported (Van der Kerk et al. 1954). The trialkyl tins show considerably more fungicidal activity than mono - and di -alkyl tins. The initial experiments of Lewis and Hedges indicated that triethyl tin was a effective antifouling toxicant for a few weeks but failed rapidly after this initial period (Lewis et. al. 1957). Comparative studies indicated that tributyl tin compounds leached more slowly and provided effective antifouling for several months. The tributyl tin moieties have a high degree of biological activity and

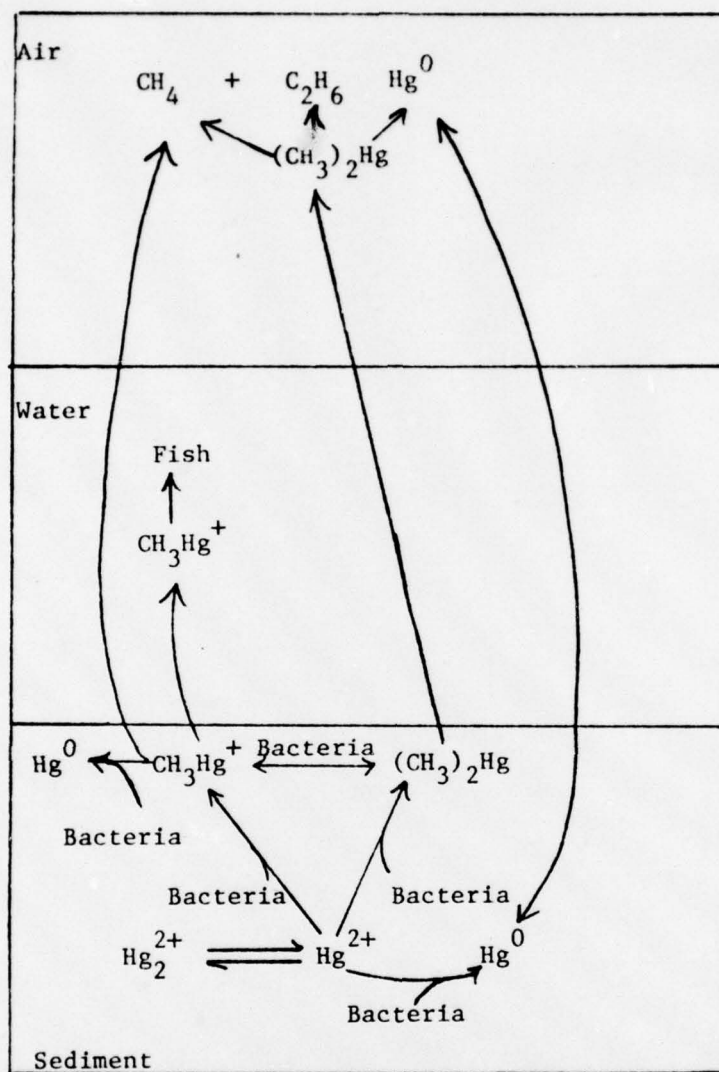


Figure 3: The Biological Cycle for Mercury
(from Wood, 1974)

toxicity studies on rats have shown that both the trialkyl and triaryl tin materials are toxic and pose certain health hazards (Piver, 1973). The higher chain trialkyls are less biologically active. The environmental degradation of the trialkyl species to innocuous inorganic tin (SnO_2) has been postulated but the mechanism has not been experimentally proven (Chapman, et. al., 1972; Willputte-Steinert et. al. 1970; Sheldon, 1975). Of the several organotin species used as antifoulants, the most commonly employed are:

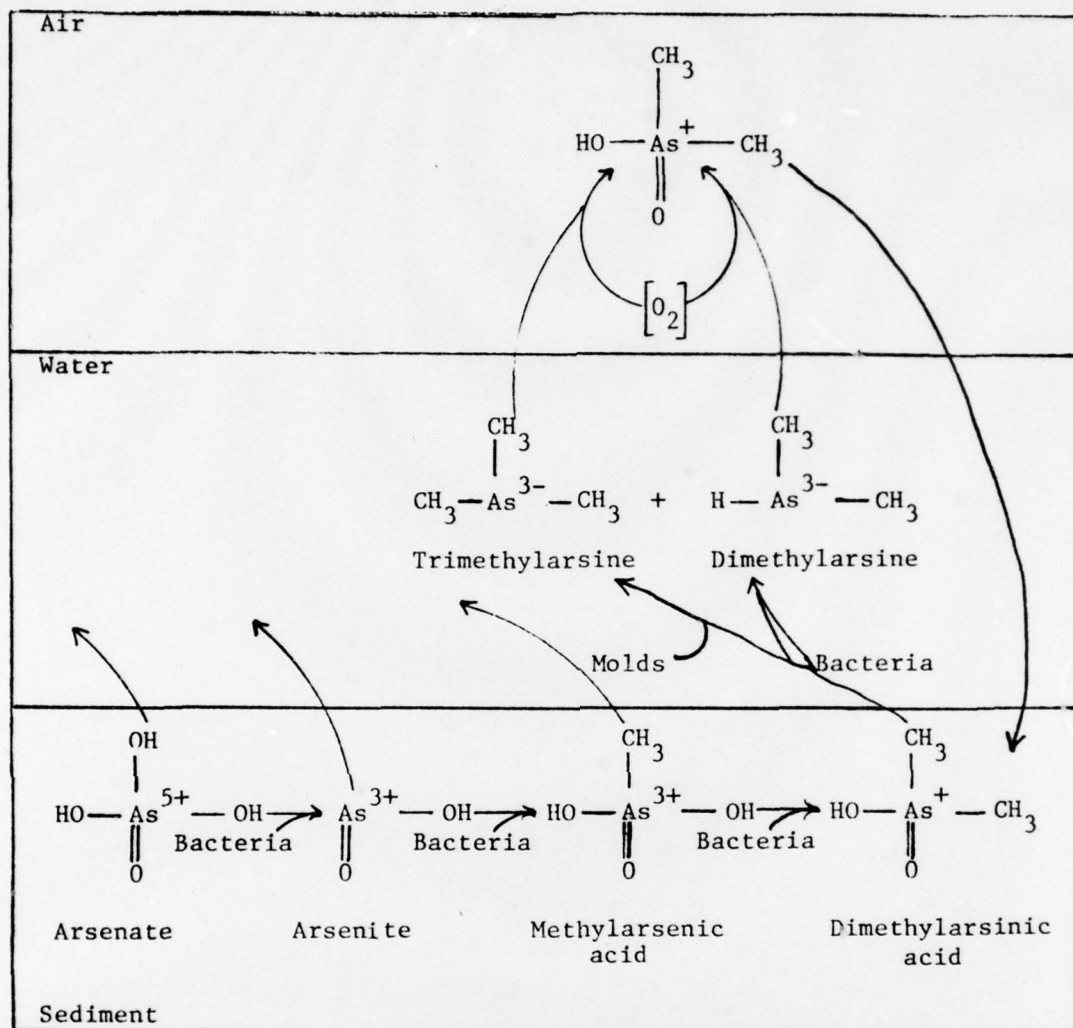


Figure 4: The Biological Cycle for Arsenic (from Wood, 1974).

(bis)tributyl tin oxide (TBTO)

tributyltin acetate (TBTAc)

tributyl tin chloride (TBTC1)

tributyl tin fluoride (TBTF)

triphenyl tin acetate (TPTAc)

triphenyl tin chloride (TPTCl)

$(\text{Bu}_3\text{Sn})_2\text{O}$

$\text{Bu}_3\text{SnOOC}^3\text{CH}_3$

Bu_3SnCl

Bu_3SnF

$\text{Ph}_3\text{SnOOCCH}_3$

Ph_3SnCl

Coatings containing the organotins exhibit both superior antifouling properties and corrosion inhibition compared to similar coatings containing inorganic mercury or copper compounds. The long lifetimes found

for these coatings is attributable to their low solubility in water, i.e. TBTC1-53ppm, TBTO-3ppm and TBTS [(bis)tributyl tin sulfide]-1ppm. Leaching rate studies for TBTO formulations have indicated that good coating performance is obtained when the binder to rosin ratio is equal to or greater than one (Baunett et. al., 1966). In acrylic antifouling paints containing organotin, it has been found that an increase in toxicant concentration lowers the antifouling lifetime of the coating. This is in direct contrast to the behavior of copper oxide coatings.

No definitive leaching mechanism has yet been established for the organotin containing coatings and no complete biological cycle for the organotins has been delineated experimentally. Work in our laboratory at the University of New Orleans is centered on developing a leaching model which can be experimentally verified in the laboratory and on speciating the organotin moieties released to the atmosphere from the use of the organotin containing coatings (Hoffman, et. al. 1978; Monaghan, et. al. 1977; O'Brien et. al. 1978; Good, et. al. 1978). Difficult analytical problems have been encountered in our attempts to determine organotin concentrations in the ppm and ppb range (Morgan et. al. 1977). However, a macroscopic leaching model has been developed which we hope will enable us to predict the minimum useful lifetimes of organotin containing coatings from laboratory leaching tests. We have also established that all of the commercially available paints which use tributyl tin compounds as toxicants, leach essentially only organotins to the environment. We have postulated that the leachate contains tributyl hydroxide as the active species (Brown, et. al. 1972; Smith, et. al. 1977). These preliminary studies and those reported by other workers indicate the need for further characterization of the environmental impact of these antifouling materials. Particular emphasis should be placed on speciation of the environmentally active organotin species, the determination of the biochemical cycle of the organotins, and the development of effective coatings having minimal leach rates.

SUMMARY

The need for effective antifouling materials for the protection of marine installations and ships in the south Louisiana area is apparent. Economic factors and long-term environmental effects must be balanced against each other in the use of chemical toxicants as antifouling agents. Coatings containing organotin toxicants appear to have very favorable economic factors but their long-term toxicological effects are yet to be determined.

ACKNOWLEDGEMENTS

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organotin toxicants. As these materials find ever increasing utility and application in the marine industry and in naval operations, their long-term environmental impact on harbors and shipyards will become more important. The assessment of this environmental insult to the wetlands areas of south Louisiana is dependent on our ability to quantify the release of toxicant to the biosphere and to follow the biochemical pathway of the toxicant from release to eventual degradation as innocuous inorganic tin.