

CHAPTER I

A WORLD-WIDE SURVEY OF SLIME FORMATION ON ANTI-FOULING PAINTS

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1.1 INTRODUCTION

Fouling results from the settlement and growth of a variety of plant and animal forms. Fouling on the hulls of ships results in an increase in frictional resistance leading to loss of speed and increased use of fuel (Townsin et al., 1981). In the past, acorn barnacles were the most troublesome fouling forms (see Southward & Crisp, 1963) but the trading patterns of modern ocean-going ships with quick turn-round periods and rapid transition between tropical and temperate waters favours the settlement of algae rather than barnacles and other animals (Christie, 1973). However, recent studies on the attachment of barnacle larvae under flowing conditions led Dalley and Crisp (1981) to conclude that the paucity of barnacles on ships with a quick turnaround was due to the short period spent in larvae-rich coastal waters rather than the inability of the cyprids to attach on moving ships. The most common fouling algae on ships are species of the green alga Enteromorpha and the brown alga Ectocarpus. The dominance of Enteromorpha results from its cosmopolitan distribution, its enormous reproductive potential and its ability to withstand widespread fluctuations in environmental conditions such as desiccation and salinity (Biebl, 1962; Christie & Shaw, 1968). Enteromorpha is commonly found to be the dominant alga on traditional copper-containing anti-fouling paints (Banfield 1980, Evans 1981). Following the introduction of organometallic biocides particularly triorganotin compounds into paints, Enteromorpha was largely replaced by Ectocarpus as the major cosmopolitan fouling alga on ships (Evans, 1970). Ectocarpus has been shown to be more resistant to triorganotin compounds than Enteromorpha (Mearns, 1973). Ectocarpus grows as a dense mat, rapidly covering a surface by means of its horizontal creeping system of filaments combined with rapid reproduction and establishment of new plants (e.g. Clitheroe and Evans, 1975; Fletcher and Chamberlain, 1975). Following the introduction of self-polishing copolymer (SPC) anti-fouling paints in the early 1970's weed fouling became less important. In SPC systems, the copolymer of tributyltin methacrylate and methyl methacrylate hydrolyses at

the paint/seawater interface releasing the biocide tributyl tin in a controlled manner. Other biocides such as cuprous thiocyanate and cuprous oxide are incorporated into the polymer matrix and these are also released as the polymer hydrolyses. The rate of hydrolysis, known as the "polishing rate", depends on a number of factors including the speed of water movement, pH and temperature. As the paint "polishes", thereby becoming smoother, the skin frictional resistance of the vessel decreases providing it remains free of fouling. On ships operating under optimal conditions the rate of biocide release should be sufficient to control all types of fouling. However, this is rarely the case and the copolymer paints become fouled by diatom slimes (Christie *et al.*, 1976; Daniel *et al.*, 1980) and occasionally by macroalgae and/or barnacles.

Microbial slime films have been shown to increase significantly the drag of objects in contact with moving seawater (Fischer *et al.*, 1984; Haderlie, 1984; Loeb, 1981; Gucinski, *et al.*, 1984). A recent study by Lewthwaite *et al.* (1985) has quantified the drag imposed by slime on a ship's hull. A slime layer of one millimeter thickness caused an 80% increase in skin friction together with a 15% loss in ship speed compared with values obtained for the clean hull.

The voyaging patterns of ships are very complex and the geographical location of the onset of fouling is rarely known. The present study was initiated to provide data on the fouling communities throughout the world particularly with respect to the distribution of slime organisms on three types of anti-fouling composition.

1.2 MATERIALS AND METHODS

1.2.1 Test Surfaces. Each test kit consisted of three plastic strips, 8 x 3cm attached to a wooden holder. Half of one strip was untreated thereby serving as a non-toxic surface whilst the other half was painted with a continuous contact vinyl-rosin conventional antifouling paint containing cuprous oxide as the only biocide. A second strip was painted with a clear varnish composed of 60% tributyl tin methacrylate and 40% methyl methacrylate and thus containing tributyl tin as the sole biocide. The third strip was painted with a self-polishing tributyl tin methacrylate/methyl methacrylate copolymer containing cuprous oxide and thus having both tributyl tin and copper as biocides. These four surfaces are referred to throughout this paper as non-toxic, copper, organotin and organotin/copper respectively. The plastic strips used were either black or white plastic so that the non-toxic and those coated with the organotin varnish appear either black or white on photographs.

1.2.2 Immersion. Sets of test panels were immersed for 2 months at a depth of approximately one metre below the water surface. On removal from the water, each holder with panels was preserved by immersing overnight in 4% (v/v) formaldehyde in seawater. Excess formaldehyde was poured away and the holder sealed in a plastic box which was sent to Birmingham for examination.

1.2.3 Sites. Fifteen sites around the world were used in the survey. The geographic co-ordinates are listed in Table 1.1. Panels were immersed and returned on a regular basis from sites 1-7 and continuous data from January 1983 - December 1984 is presented for these sites. Panels from sites 8-15 were returned intermittently and a full set of data is not available.

TABLE 1.1

Geographical co-ordinates of test sites

Site No.	Site/ Country	Geographical		Number of Samples
		Lat.	Co-ordinates Long.	
1	Miami/U.S.A.	25°45'N	80°15'W	13
2	Rio-de-Janeiro/Brazil	22°53'S	41°17'W	14
3	Newton Ferrers/England	50°18'N	4°02'W	18
4	Burnham/England	51°31'N	0°49'E	16
5	Dubai/United Arab Emirates	24°59'N	55°00'E	14
6*	Tamano/Japan	34°29'N	133°56'E	15
7*	Aioi/Japan	34°44'N	134°23'E	15
8	San Francisco/U.S.A.	37°48'N	122°22'W	8
9	La Spezia/Italy	44°07'N	9°48'E	7
10	Bratton/Sweden	57°55'N	11°45'E	9
11	Djuro/Sweden	59°29'N	18°40'E	6
12	Singapore	1°24'N	103°59'E	8
13	Hong Kong	22°22'N	114°15'E	2
14	Kaosiung/Taiwan	22°36'N	120°17'E	4
15	Sydney/Australia	16°40'S	139°30'E	9

*Tamano and Aioi are both located on the Inland Sea, approximately 80km apart.

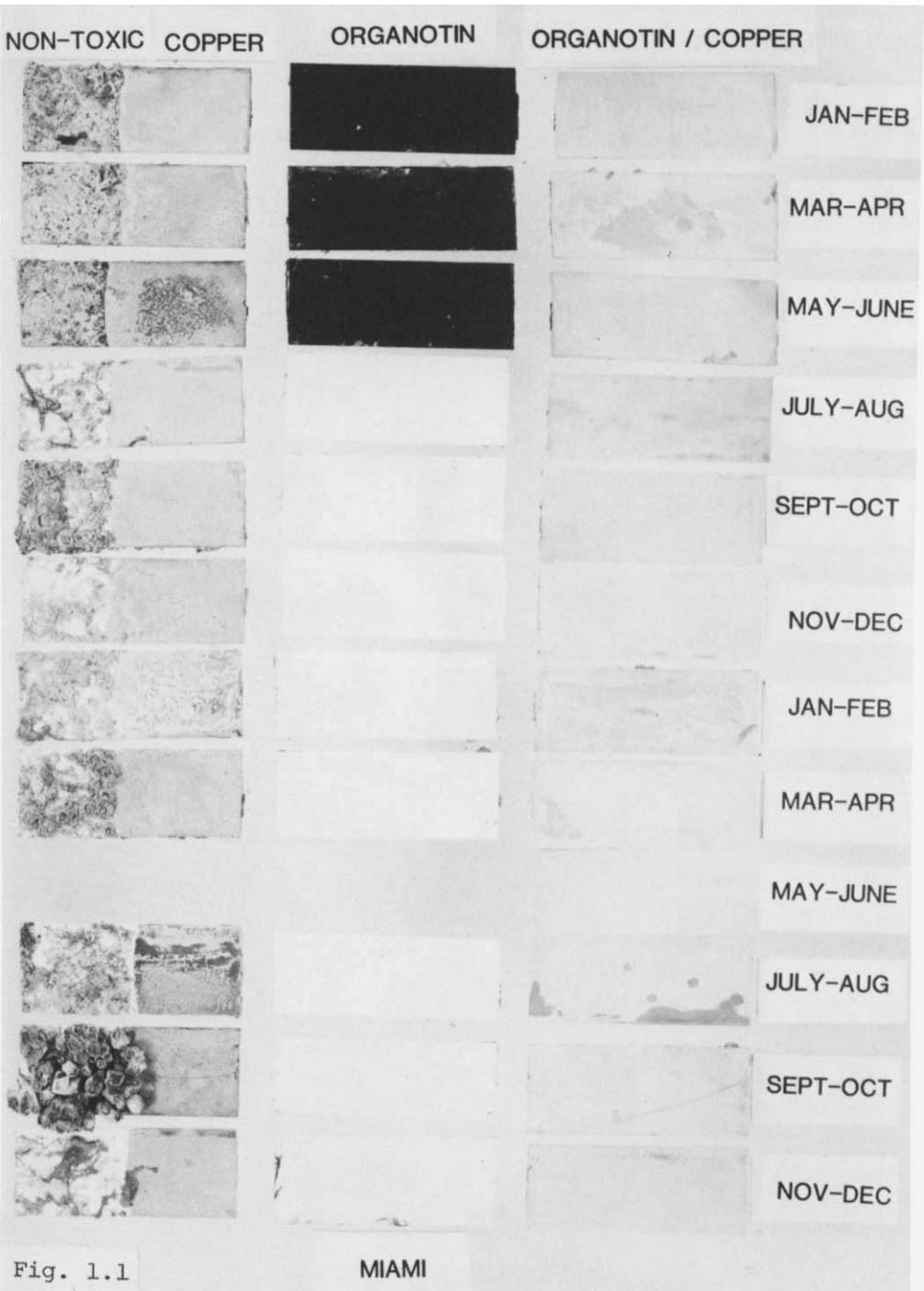
1.3 RESULTS

The panels from sites 1-7 between January 1983 and December 1984 are shown in figures 1.1-1.7. Preliminary data from January-December 1983 were reported in Callow (1984).

Miami: The panels from Miami are shown in Fig.1.1; the May-June 1984 panels were lost. All panels were covered by a fine deposit of silt (as evidenced by the poor contrast of Fig.1.1). The mean surface seawater temperatures recorded at the exposure site were 22°C over the winter months (Dec-Feb) and 27°C over the summer months (June-August). Barnacle (B. amphitrite) settlement occurred throughout the year, peak settlement being during September and October. Macroalgae grew vigorously on all non-toxic panels but were not found on any of the anti-fouling formulations. The most abundant macroalgae were Cladophora sericea, Ectocarpus siliculosus, Callithamnion sp. and Enteromorpha intestinalis. The anti-fouling surfaces supported only light diatom slimes. The organotin/copper paint bore only patches of Amphora slime (A. coffeaeformis, A. veneta and A. bigibba) whilst on the copper paints more substantial slimes of Amphora spp. mixed with Amphiprora and Stauroneis were found. Slimes of Achnanthes angustata occurred on the organotin varnish panels during the winter months.

Rio-de-Janeiro: The panels from Rio-de-Janeiro are shown in Fig.1.2; the July-August 1984 samples were lost. Water temperatures range between 21°C (June-August) and 27°C (November-January). Heavy animal fouling occurred on all the non-toxic panels. The major types in order of abundance were barnacles (B. amphitrite and B. tintinnabulum), the hydrozoan Obelia geniculata, the polyzoan Bugula neritina, the serpulid worm Hydroides norvegica, and the amphipod Jassa falcata. Algae were not found on the non-toxic control with the exception of a microscopic growth of Ulothrix and filamentous blue-green algae (Cyanobacteria). All three anti-fouling surfaces allowed settlement and growth of both species of barnacle although in reduced numbers compared to the controls. All antifouling surfaces bore diatom slimes together with substantial growths of the protozoan Vorticella. Both the copper and organotin/copper paints had slimes dominated by Amphora (A. coffeaeformis and A. veneta) and Amphiprora. The sole diatom found on the organotin varnish was Achnanthes longipes.

Newton Ferrers: The panels from Newton Ferrers are shown in Fig.1.3. Mean surface water temperatures are 8°C for December-February and 16°C for June-August. Growth on the control surfaces was negligible during the winter (November-February) and was unusually light during the whole of 1983. The non-toxic panels predominantly bore ectocarpacean algae (Ectocarpus siliculosus and Giffordia granulosa) during the summer months. These were intermixed with the hydrozoan Tubularia indivisa between July and October. Other algae present in lesser numbers included Enteromorpha intestinalis, Ulothrix flacca, Ulva lactuca, Polysiphonia elongata and Ceramium rubrum as well as small numbers of a mixed population of diatoms. During 1984 patches



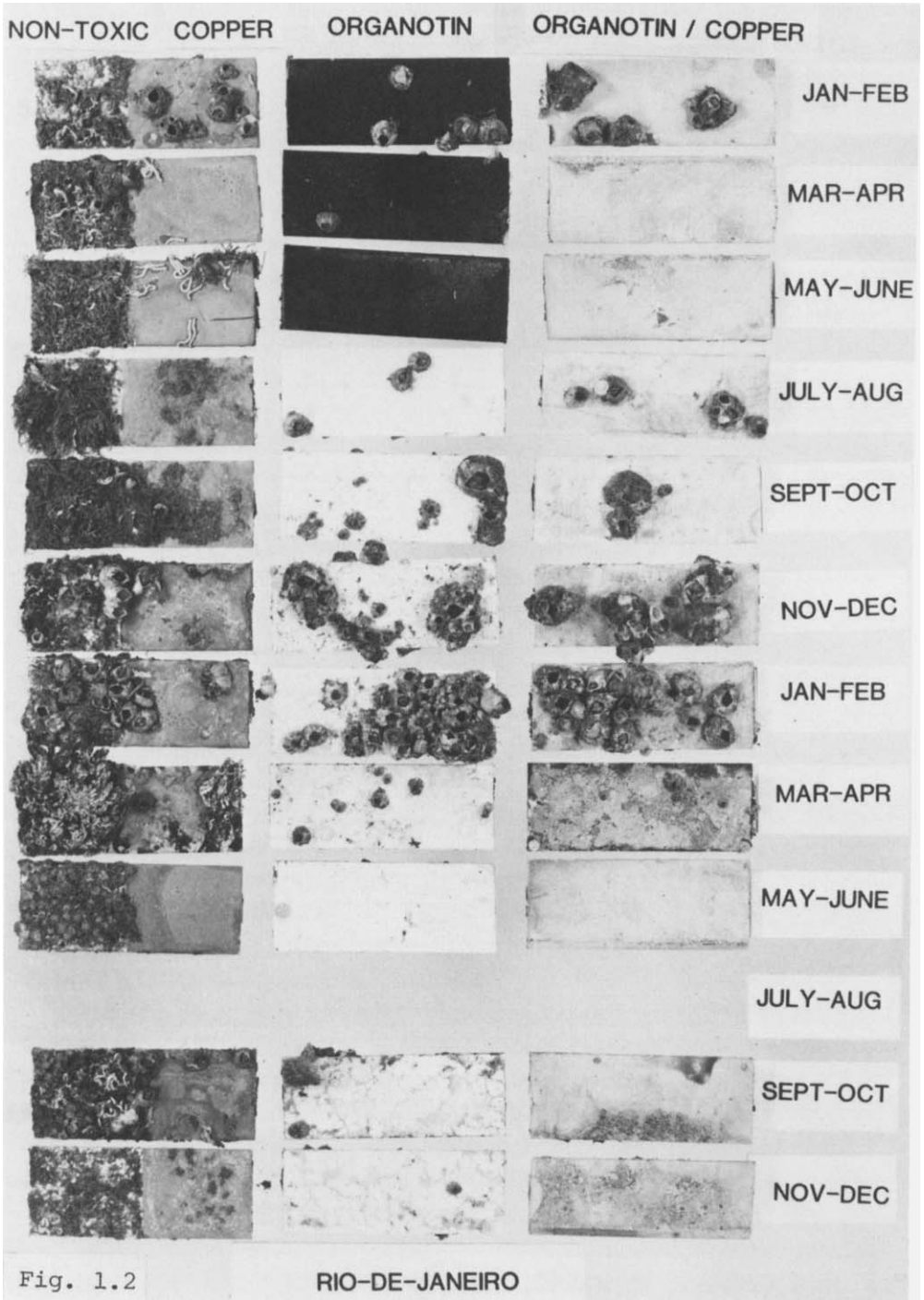
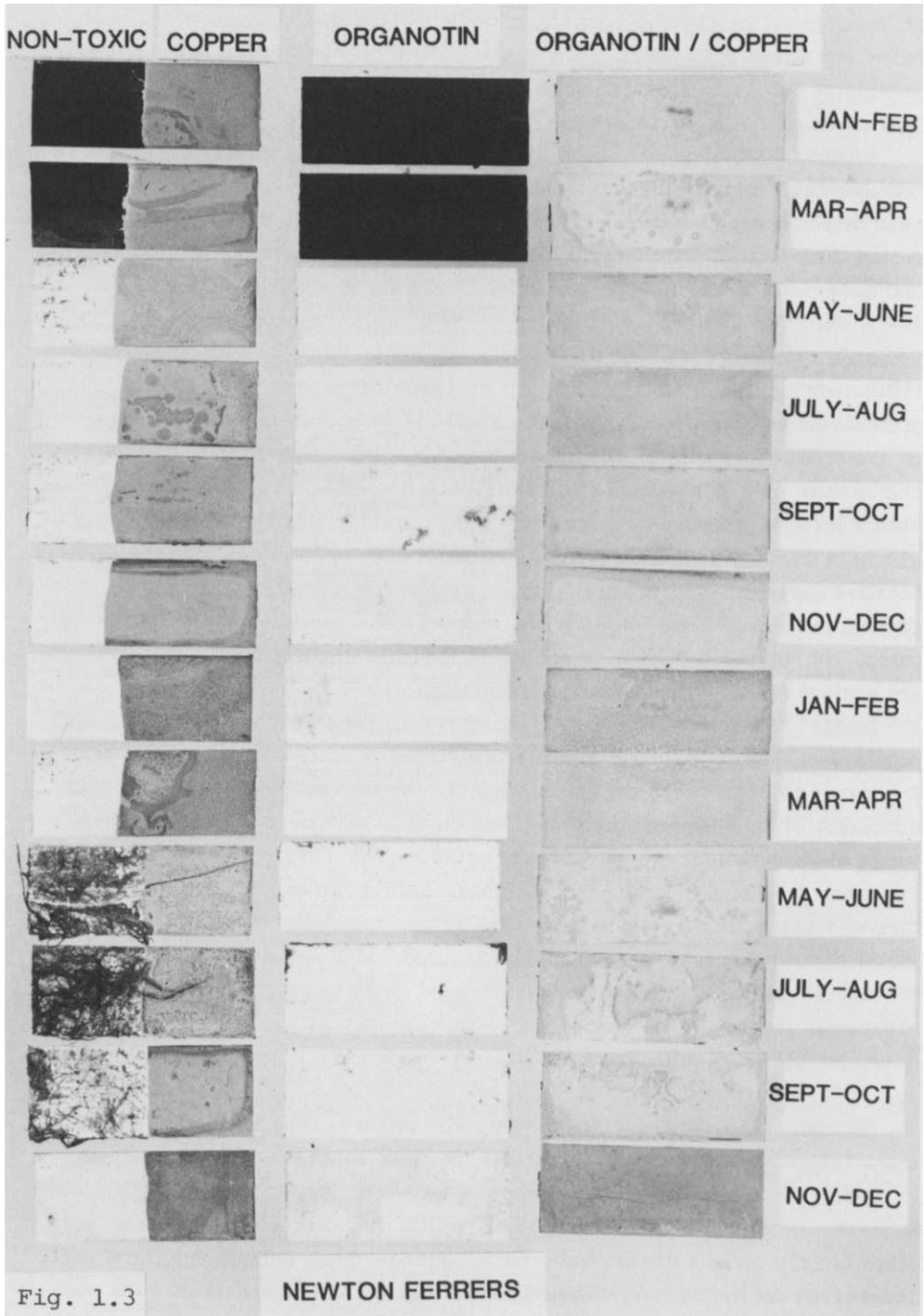


Fig. 1.2

RIO-DE-JANEIRO

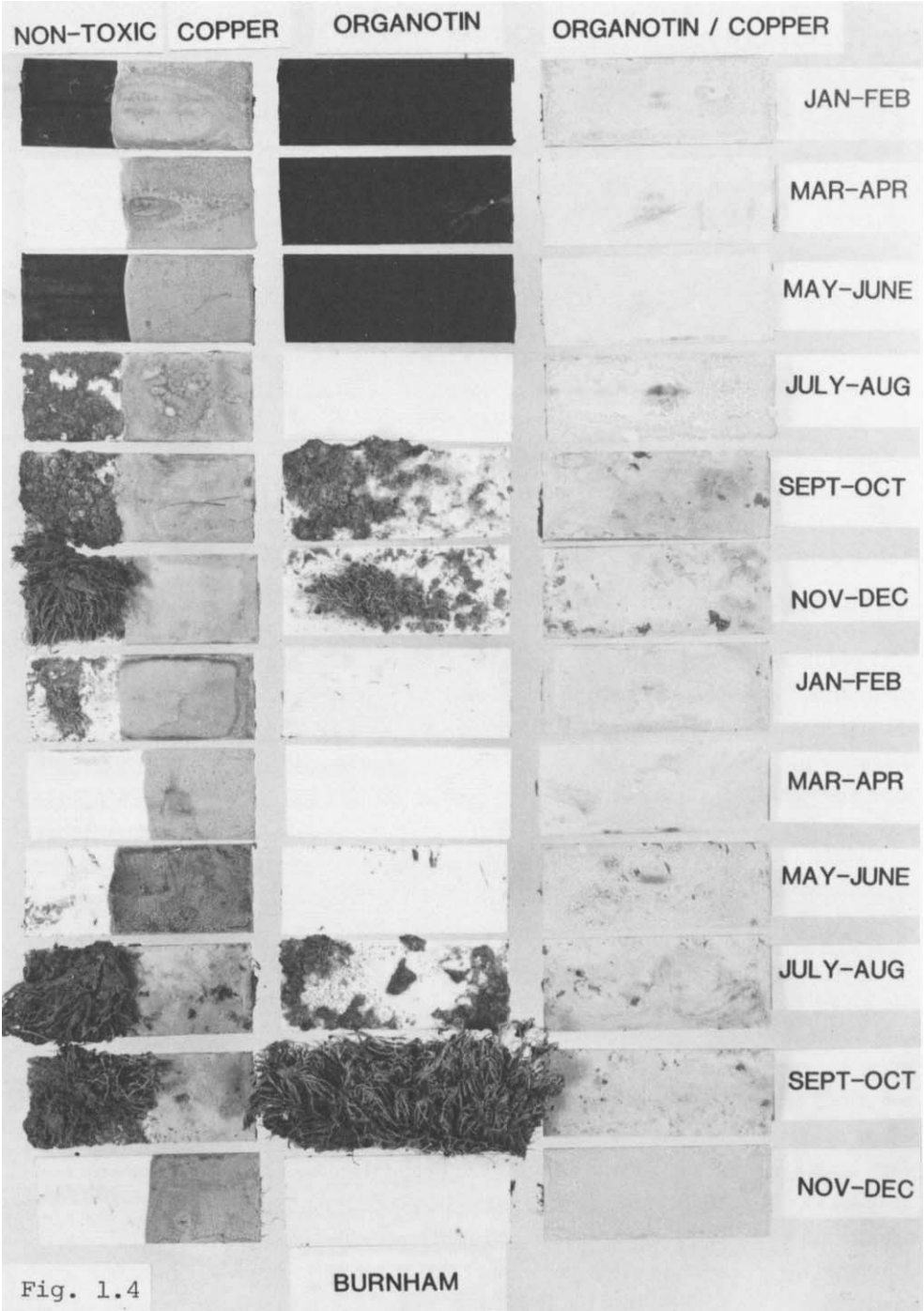


of Amphora (A. veneta and A. coffeaeformis) colonized the organotin/copper paint and these plus Amphiprora hyalina grew on the copper paint. Small growths of Tubularia indivisa were found on the organotin varnishes and during 1984 patches of Achnanthes subsessilis were also present.

Burnham: The panels from Burnham are shown in Fig.1.4. There is considerable variation in water temperature between the winter months with a mean of 6°C during November-February and summer months with a mean of 20°C during June-August. This rapid increase in water temperature during spring and summer is due to large areas of mud and sand being exposed to the sun at low tide. The seasonal settlement of the Australian barnacle, Elminius modestus typically occurred during July-August followed by settlement of the hydrozoan Tubularia indivisa. Both of these organisms were found in the presence of the amphipod Jassa falcata and all were able to colonize and grow on the organotin varnish. Small amounts of algal fouling occurred throughout the summer on the non-toxic and organotin surfaces. The most frequently encountered algae were Enteromorpha intestinalis, Ectocarpus siliculosus, Ulothrix flacca, Ceramium rubrum, Polysiphonia sp. and the tube-dwelling diatoms Navicula (Schizonema) ramosissima and N. pseudocomoides. Various fouling organisms were found on the copper and organotin/copper antifouling paints but in reduced numbers including Navicula ramosissima, Jassa falcata and a mixed Amphora veneta/Amphiprora hyalina slime.

Dubai: The panels from Dubai are shown in Fig.1.5: the March-April 1983 panels were lost. The water temperature ranged from 23°C (mean for December-February) to 37°C (mean for June-August). No obvious seasonal settlement occurred. The major fouling organisms on all the non-toxic control panels were blue green algae (Cyanobacteria). The following genera were represented:- Oscillatoria, Gleotrichia, Calothrix and Spirulina. Other common fouling forms were Balanus amphitrite, ascidians and the green algae Percursaria percursa, Enteromorpha flexuosa and E. linza and Derbesia sp.. The latter and blue green algae were found in reduced growth forms on the organotin varnish. The copper and organotin/copper paints supported the growth of diatom slimes principally composed of Amphora veneta and Amphiprora sp..

Tamano: The panels from Tamano are shown in Fig.1.6. This site is characterised by heavy algal fouling. The mean winter water temperature is 11°C (December-February) and the mean summer water temperature is 24°C (June-August). On the non-toxic surface algae are abundant throughout the year often tightly bound with the mud-binding amphipod Jassa falcata and these were intermixed during January-February with a growth of hydrozoans. The most abundant macroalgae were Ectocarpus fasciculatus, Enteromorpha intestinalis,



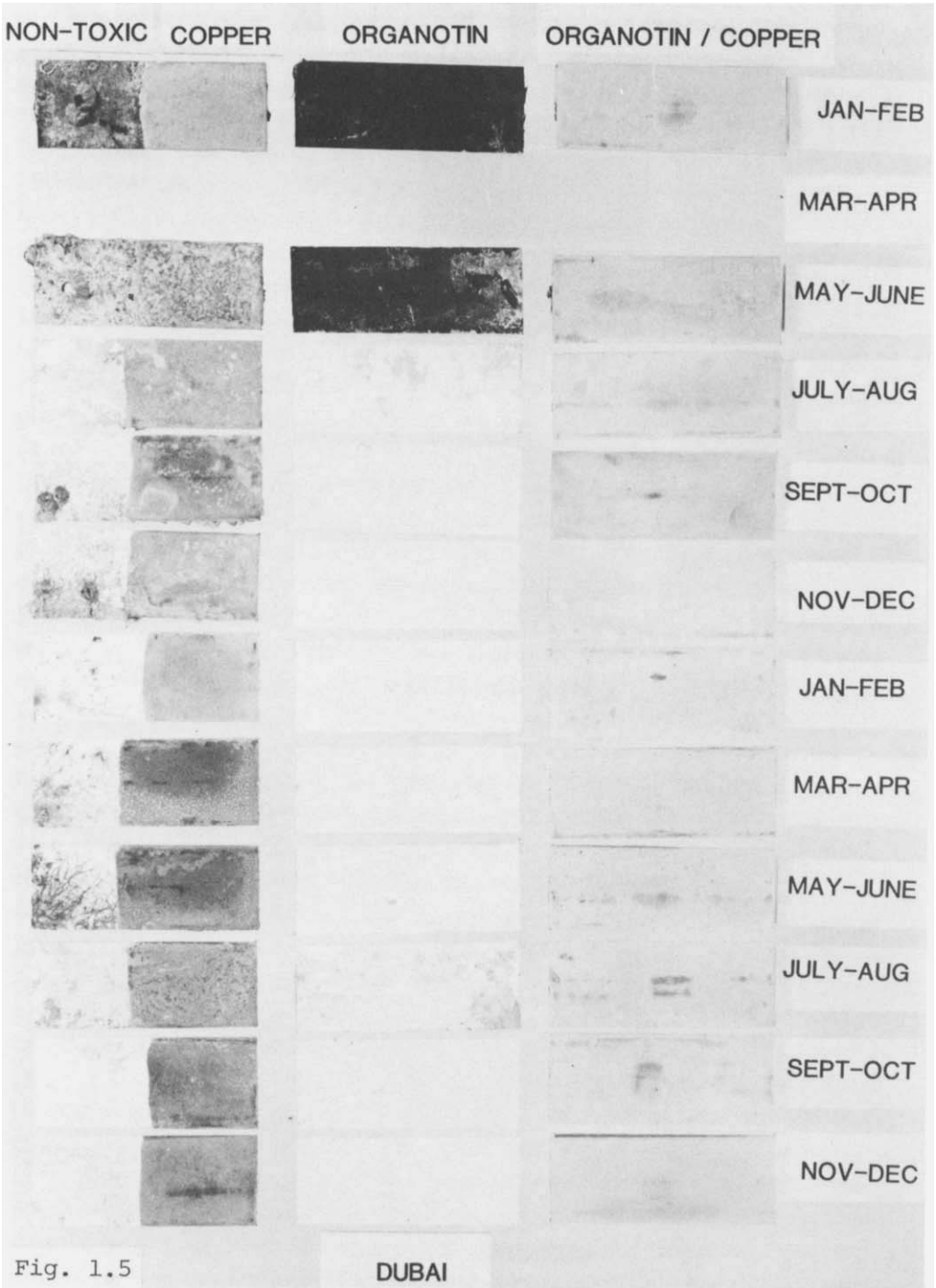


Fig. 1.5

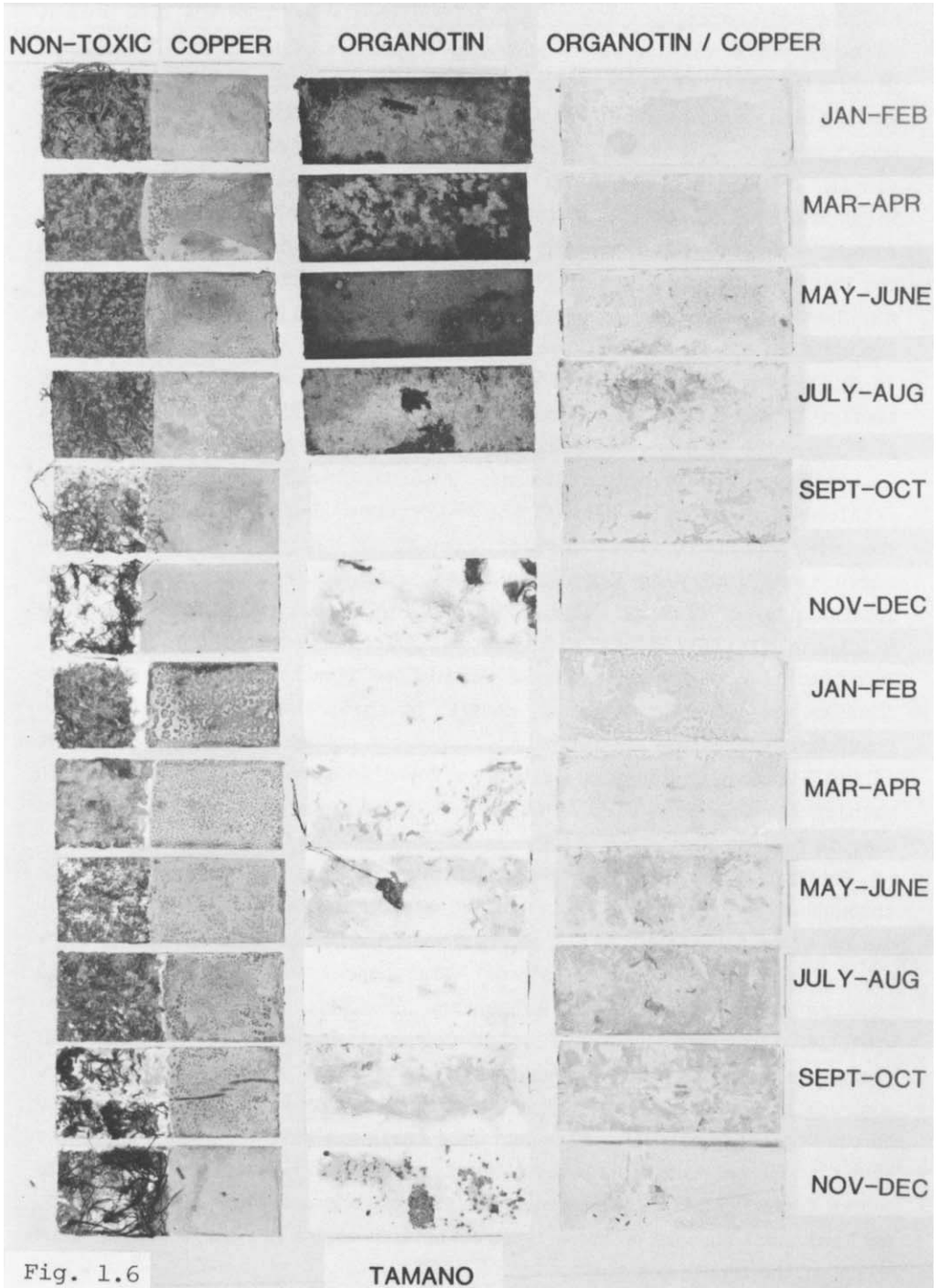
DUBAI

E. linza and Cladophora sericea. A species-rich diatom slime was also present including members of the genera Navicula, Stauroneis, Fragilaria, Lichmophora, Nitzschia, Striatella, Melosira, Cocconeis, Achnanthes and Coscinodiscus. Thick diatom slimes were formed on all the anti-fouling surfaces. On the copper and organotin/copper paints slimes were chiefly composed of Amphora (A. veneta, A. coffeaeformis, A. sp.) and Amphiprora sp. with lesser amounts of Nitzschia ovalis. On the organotin varnish slimes of Achnanthes longipes formed, sometimes in conjunction with Jassa falcata. The mud associated with the latter could form a substrate for attachment of macroalgae as shown in the May-June 1984 sample where Enteromorpha intestinalis is attached to mud deposited on the surface of the organotin varnish.

Aioi: The panels from Aioi are shown in Fig.1.7. Water temperatures are similar to those found at Tamano although other conditions are different. At Aioi the water is deep, clear and still in comparison to the shallow, turbid, fast flowing conditions at Tamano. Aioi is characterised by its heavy settlement of barnacles between May and October. During winter and spring (November-April) fouling was chiefly due to the amphipod Jassa falcata and macro-algae including Ectocarpus fasciculatus, Ulva sp., Enteromorpha intestinalis, E. flexuosa Polysiphonia spp., Cladophora rupestris, C. sericea, Blidingia minima, and filamentous blue-green algae (Cyanobacteria). Throughout the year a diversity of benthic and planktonic diatoms were also found on the non-toxic surfaces. Members of the genera Amphora, Amphiprora, Stauroneis and Nitzschia formed slimes on the copper and organotin/copper paints. Achnanthes longipes was always found in abundance on the organotin varnishes and on some samples barnacles, Ectocarpus fasciculatus, and the diatoms Amphora veneta and Stauroneis sp. also occurred.

San Francisco: Growth on the non-toxic surface was approximately constant throughout the year. The major growth was a thick and floristically rich diatom slime intermixed with Ectocarpus siliculosus and Ulothrix flacca. The most common types of diatom in order of abundance were Melosira, Navicula (Schizonema) ramosissima, Achnanthes longipes, Navicula (Schizonema) grevillei, Gyrosigma, Nitzschia ovalis, Cocconeis, Lichmophora, Campylodiscus, Fragilaria, Grammatophora and Amphora. A thin diatom slime covered the three anti-fouling compositions. Achnanthes longipes grew as an almost pure stand on the organotin varnish. Although only small numbers of Amphora spp. were found on the non-toxic surface, A. coffeaeformis var. coffeaeformis and A. veneta formed a slime on the organotin/copper paint and these plus Amphiprora spp. and small numbers of those types identified on the non-toxic surface were found on the copper paint.

La Spezia: Most of the non-toxic panels bore a substantial growth of the



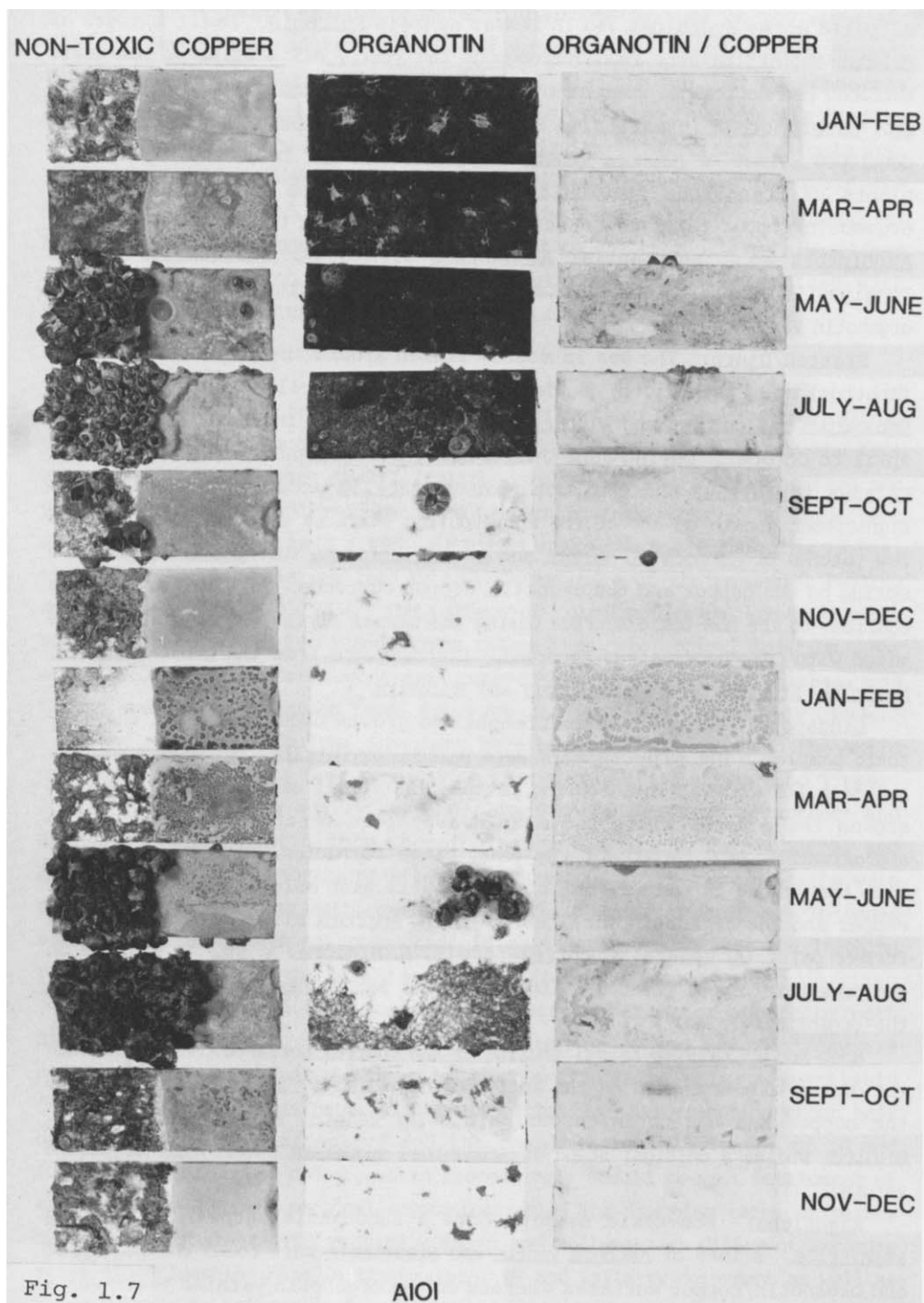


Fig. 1.7

AIOI

serpulid worms Hydroides and in lesser numbers Spirobis. Small numbers of Balanus amphitrite were found throughout the year. All samples of non-toxic surfaces had macroalgae present including Ectocarpus fasciculatus, Sctyosiphon sp., Enteromorpha intestinalis and Chaetomorpha linum. The copper paint developed slimes of Amphora veneta and Stauroneis sp. intermixed with small plants of Ectocarpus fasciculatus and Enteromorpha intestinalis. The organotin/copper paint supported little growth other than a few patches of Amphiprora sp. Substantial Achnanthes slimes (A. subsessilis and A. longipes) mixed with small plants of E. fasciculatus developed on the organotin varnish.

Bratton/Djuro: The sea is mostly frozen around the coast of both West (Bratton) and East (Djuro) Sweden from December until March. At Bratton Ectocarpus siliculosus and Ulothrix flacca grew on the non-toxic surface from April to October. During June-July a heavy settlement and rapid growth of Balanus improvisus and the protozoan Vorticella occurred. There was no significant growth on any of the anti-fouling surfaces examined except for a few patches of Amphora (A. veneta and A. coffeaeformis var. perpusilla) in the spring on the copper and the organotin/copper surfaces. At Djuro growth was confined to the non-toxic surface during the summer months when a diatom slime mixed with Chaetomorpha was recorded. Diatoms were from the genera Amphora, Navicula, Stauroneis, Coscinodiscus and Melosira.

Singapore: Heavy animal settlement and growth occurred on all the non-toxic samples. The major animals were Balanus amphitrite, colonial ascidians and serpulid worms. This fouling pattern is typical of the tropical waters around the equator where the mean seawater temperature at 1m depth is approximately 29°C throughout the year. Some barnacles, usually of smaller size than those on the non-toxic surface were also able to grow on both the copper and the organotin surfaces. A thick Amphora slime developed on the former paint (A. veneta, A. coffeaeformis, A. bigibba, A. sp.) as well as on the organotin/copper paint. A light slime of Achnanthes subsessilis grew on the organotin varnish.

Hong-Kong: Massive animal fouling of the control surfaces contrasted with the diatom slimes formed on the anti-fouling paints. Amphora slimes covered the copper and organotin/copper paints (A. veneta, A. coffeaeformis, A. bigibba) whilst a unialgal stand of Achnanthes angustata covered the organotin varnish.

Kaohsiung: Non-toxic samples bore a substantial growth of Balanus amphitrite. Slimes of Amphora veneta and Stauroneis were found on the copper and organotin/copper surfaces whereas on the organotin varnish there was a slime of Amphiprora, Stauroneis, Navicula and Achnanthes longipes.

Sydney: Moderate fouling occurred throughout the year on the non-toxic panels. Serpulid worms from the genera Hydroides and Spirobis were present throughout as were the algae Ectocarpus siliculosus and Enteromorpha intestinalis. A mixed population of diatoms was also found on all samples including Stauroneis, Amphora coffeaeformis, Amphiprora and Navicula spp. Thick diatom slimes developed on all the anti-fouling surfaces throughout the year. The copper and organotin/copper paints had slimes of Amphiprora, Stauroneis, Amphora veneta and Navicula whilst on the organotin varnish slimes of Achnanthes (A. longipes and A. angustata) sometimes intermixed with Stauroneis and Amphiprora were most commonly found.

1.4 DISCUSSION

Fouling growth on non-toxic submerged surfaces can be immense even within two months as seen at certain sites in the present study. Although the test areas employed were very small, fouling development was consistent from one year to the next and followed the same pattern as that observed on large test areas immersed at certain sites. At sites where the spore inoculum is low, the use of small panels may lead to an underestimate of the potential fouling community (see Brecka, 1983). The pattern of colonization and growth appears to be related more to local conditions rather than geographical location. For example, large differences were seen between Newton Ferrers and Burnham, and Tamano and Aioi even though these sites are geographically relatively close.

Many surveys of fouling organisms have been undertaken around the world over the last 30 years (see Anon, 1952; Fletcher, 1974; Costlow and Tipper, 1984) and the present survey has underlined the widespread occurrence and abundance of the most common macrofoulers viz. Balanus, Enteromorpha and Ectocarpus. At the majority of sites, all three antifouling compositions were effective in preventing settlement and growth of these organisms. In cases where colonization was not prevented, it must be concluded that the leaching rate of biocides from the paints was not sufficiently great.

The paints tested here contained either copper or organotin or both organotin and copper. Copper leaching rates of 10 and 20ug/cm²/day are required to prevent settlement of barnacles and diatom slime respectively (Banfield, 1980). It is generally accepted that for triorganotins about half of these values are effective and the combined leaching rates of 10 and 4ug/cm²/day for copper and organotin respectively should prevent settlement of all organisms (Milne, personal communication). The leaching rates of paints used in this study are not precisely known and will vary at different exposure sites since leaching rate is temperature, pH and salinity dependent as well as being related to the speed of water movement in the case of copolymer paints.

During the first two months after immersion and under dynamic conditions at 25°C the following leaching rates are expected: >10ug/cm²/day copper from the copper paint; approximately 2.5ug/cm²/day tributyltin from the organotin varnish and 10 plus 2.5 ug/cm²/day of copper and tributyltin respectively from the organotin/copper paint (Milne, pers. comm.). French *et al.*, (1985) quote copper leaching rates of 20-30 ug/cm²/day from a copolymer paint after two months immersion on a raft but tributyltin leaching rate was not determined. Therefore, it would be expected that sufficient copper and tributyltin would leach from the copolymer paint used in this study to prevent all macrofouling. Furthermore, any organisms able to colonize this surface will be highly resistant to copper and triorganotin.

The occurrence of the major fouling organisms found on the three anti-fouling formulations are listed in Table 1.2. The majority of cases of animal fouling occurred at Rio-de-Janeiro and here, even the organotin/copper paint allowed settlement of barnacles. Local conditions such as high pollution may result in reduced rates of biocide leaching at this site. There is a high incidence of diatom slimes on all antifouling surfaces but with a restricted species composition (see Robinson *et al.*, 1985). *Amphora* and to a lesser extent *Amphiprora* were found on the majority of panels containing copper or organotin/copper, and a proportion of panels at every site bore slimes of one or both diatoms. The dominance of slimes of *Amphiprora paludosa* and *Amphora coffeaeformis* on panels of SPC paints containing cuprous oxide was also noted by Robinson *et al.*, (1985). Species of both *Amphora* (Daniel and Chamberlain, 1981; French, 1985) and *Amphiprora* (French, 1985; Sanders *et al.*, 1981) are known to be highly resistant to copper. Daniel and Chamberlain showed that copper resistance in *Amphora veneta* was due to immobilization of copper within intracellular membrane-bound bodies thereby keeping cytoplasmic levels low. Although *Amphora* and *Amphiprora* were found on the organotin/copper paint they were rarely found on the organotin varnish whilst *Achnanthes* slimes were found on 50% of the latter panels. Three species of *Achnanthes* were found viz. *A. longipes*, *A. subsessilis* and *A. angustata*. *A. longipes* is reported to be resistant to copper (Hendey, 1951; Blunn, 1982). In laboratory measurements of LC50 values for tributyltin oxide, *A. longipes* was found to be only slightly (20%) more resistant than *Amphora coffeaeformis* var. *perpusilla* (Wood, pers. comm.). *Achnanthes subsessilis* on the other hand is known to be highly resistant to organotins (Callow and Evans, 1981) and the LC50 value is fifteen times higher than that for *A. longipes*. The differences seen in species composition of slimes between the organotin and organotin/copper surfaces cannot be explained solely in terms of current data on resistance to copper and organotin.

TABLE 1.2

Incidence of major fouling organisms on anti-fouling surfaces

ORGANISM	COPPER	ORGANOTIN/COPPER	ORGANOTIN
Barnacles	13	8	24
Other animals	18	0	17
<u>Enteromorpha</u>	5	0	8
<u>Ectocarpus</u>	4	0	18
Other macro-algae	0	0	4
<u>Amphora</u>	101	107	5
<u>Amphiprora</u>	67	47	7
<u>Stauroneis</u>	33	17	12
<u>Navicula</u>	14	14	9
<u>Nitzschia</u>	11	9	2
<u>Achnanthes</u>	0	0	81
Other diatoms	6	0	6

A total of 158 panels of each surface were examined.

TABLE 1.3

Incidence of fouling organisms on "in-service" ships*

ORGANISM	ANTIFOULING PAINT	
	COPPER ⁺	ORGANOTIN/COPPER ⁺⁺
Barnacles	8	1
<u>Enteromorpha</u>	11	4
<u>Ectocarpus</u>	5	6
Other macro-algae	5	2
<u>Amphora</u>	5	18
Other diatoms	10	12

*Fouling samples from a total of 34 ships were examined

⁺11 ships were coated with a conventional copper antifouling paint

⁺⁺23 ships were coated with a self-polishing copolymer paint containing organotin and copper

Patches of the three antifouling paints used in this survey are currently being tested on bilge keel panels attached to an in-service ship. It will be of interest to discover whether the organotin varnish becomes slimed with Achnanthes under ship-operating conditions. Both the copper and organotin/copper paints are widely used on ships. Results from a survey of paint flakes taken from in-service ships (Callow, in preparation) is summarised in Table 1.3. The organisms identified on the conventional copper paints are predominantly macrofouling types whilst the majority of copolymer paints bear only diatom slimes. Amphora is the most common slime diatom and the three most commonly occurring species are the same as those found on the panels in the present study viz. A. veneta, A. coffeaeformis, A. bigibba. However, Amphiprora, Stauroneis, Achnanthes, Navicula and Nitzschia have all been found as major ship-fouling diatoms. Thus, the composition of slimes which develop on static panels and on in-service ships appear to be similar.

Further laboratory studies on biocide resistance (particularly using mixed combinations of biocides) are needed on those diatoms found to flourish on antifouling paint surfaces. Such data combined with analysis of paint leachates will improve our understanding of the biology of fouling organisms.

1.5 ACKNOWLEDGEMENTS

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