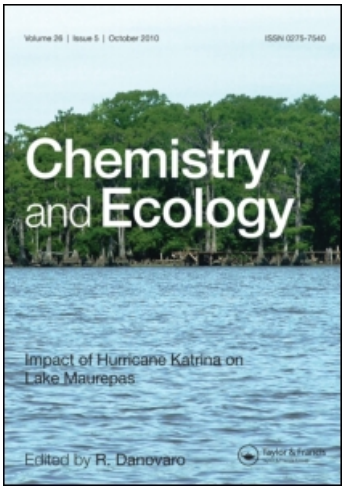

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Effect of Polymeric Coatings On Phytoplankton Standing Crop

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EFFECT OF POLYMERIC COATINGS ON PHYTOPLANKTON STANDING CROP

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Some polymeric marine coatings based on vinylcopolymer and linseed oil have been prepared in the laboratory and their efffect on phytoplankton standing crop was tested. The coating is prepared either from vinylcopolymer or linseed oil or a mixture of both binders with 1:1, 1:2 and 2:1 ratios in the presence or absence of a soluble resin. The coatings were applied to glass slides and tested in a sea water medium. Also, correlations between the weight of the coating film and numbers of phytoplankton species were calculated. The results showed no correlation between the weight of films of either vinylite or oil binders and the total number of all phytoplankton species, but significant correlation was found for some phytoplankton species, such as *Thalassiosira decipiens*.. The weight of the film coating of vinylcopolymer in the presence of soluble resin with 1:1, 1:2 and 2:1 ratios is significantly correlated to the total number of phytoplankton and some other dominant species. Formulations of linseed oil and a soluble resin with 1:1, 1:2 and 2:1 ratios are correlated to the numbers of *Chaetoceros affinis*, *Bellorochea malleus* and *Skeletonema costatum*.

KEY WORDS: Coatings, vinylcopolymer, oil, phytoplankton, marine environment.

1 INTRODUCTION

Vinylcopolymer and linseed oil are widely used in marine paints. The protection of both binders against marine corrosion of steel surfaces has been tested (Tadros, 1991). The test showed that linseed oil based paint gave protection to the steel surface for 6 months, while a vinylcopolymer coating in the presence of soluble resin gave a shorter protection. The addition of soluble resin material to an oil base of paint impairs paint film properties, while resin improves protection if added in a certain fraction to vinylcopolymer formulations. The protection of these two binders against biofouling by phytoplankton has not been tested in our local waters. Phytoplankton and its constituent species in Alexandria Harbour water varies according to the water conditions (Zaghlour *et al.*, 1990 and 1991). Phytoplankton species are greatly affected by nutrient salts, particularly phosphate and silicate concentrations which lie in the ranges 0–26.4, 0–874 $\mu g\ l^{-1}$ respectively. The monthly change in water constituents of Alexandria Eastern and Western Harbours is due to the huge discharges of industrial, agricultural and domestic waste water (Neesim and Tadros, 1992). The attachment of epiphyte on a submerged substrate in sea water starts with filamentous forms after nearly 24 hr

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immersion, followed by benthic forms of diatoms, then protozoans, and eventually the colonisation by crustaceans appears along with other macro fouling organisms.

In the present work, different polymeric coatings based on vinylite and linseed oil were prepared. Each binder was tested alone and in the presence of the other binder in the presence of soluble resin material. The coatings are applied to glass slides and the weight of the films measured. The effect of these film coatings on numbers of phytoplankton was studied by the immersion of the slides in a natural sea water medium, and the dominant species found in the media and on the slides were counted. In addition, the sea water media was analysed for nutrient salts, oxidizable organic matter, dissolved oxygen, alkalinity. pH and temperature were also measured.

2 METHODS

2.1 Slide Preparation

Glass slides were used with dimensions (7.6 × 2.7 × 0.15 cm). They were first cleaned with laboratory detergent and a potassium dichromate/sulphuric acid cleaning solution to remove contaminants. After rinsing with acetone, the slides were heated in an oven at 100°C.

2.2 Preparation of Polymeric Coatings

Two types of binders were used in coatings, vinylcopolymer and linseed oil. Each was tested either alone, or in the presence of a soluble resin or mixtures of both binders in different ratios, these forming a total of twelve coatings (Table I). The film forming solutions were made by dissolving the appropriate amount of the binders in and a soluble resin material in a suitable blend of solvents. Three replicate slides for each mixture were prepared for inspection after 7, 10 and 14 days. The slides were left to dry one week before immersion in sea water media in the laboratory. Each coating composition was tested twice over two successive months. The weight of the dry films was also determined (Table I).

2.3 Sea Water Immersion Test

Each glass slide was immersed in about 600 ml of sea water placed in all glass bottle. The slide was then placed with one edge on the bottom of the bottle and with the top resting against the side. A separate bottle was used for each test slide. The control was sea water medium without slide immersion and was analyzed immediately after sampling to identify phytoplankton and for the characteristics listed in Table III (dissolved oxygen, alkalinity, organic matter, nitrite-N, phosphate-P, ammonia-N, SiO_2–Si, and salinity). A blank control at each time of inspection (7, 10 and 14 days) was provided by an untreated glass slide immersed in the same way in 600 ml sea water. This test was repeated monthly from September 1991 to July 1992. The type of polymeric coatings tested in each of the eleven months is shown in Table I. Every month and at the end of each specified observation time, the slides were removed from

Table I Composition of polymeric coatings and the weight of their paint films.

Coating composition	*Abbrevation and ratio*	*Immersion time (date at start)*	*Inspection time (days) weight of paint film (g)* 7	10	14
Vinylcopolymer	V alone	22.09.91	0.0617	0.0472	0.0507
Vinylcopolymer	V alone	22.10.91	0.0575	0.0498	0.0819
Linseed oil	L alone		0.1613	0.1454	0.1554
Vinylcopolymer	V alone	24.11.91	0.1934	0.1920	0.1996
Linseed oil	L alone		0.3364	0.1999	0.2218
Vinylcopolmer + Linseed oil	V + L 1:1		0.0874	0.1841	0.1558
Vinylcopolymer	V alone	29.12.91	0.0789	0.0887	0.0896
Linseed oil	L alone		0.2178	0.1963	0.2090
Vinylcopolymer + Linseed oil	V + L 1:1		0.2278	0.2391	0.2270
Vinylcopolymer + soluble resin	V + R 1:1	23.01.92	0.0913	0.1104	0.1198
Linseed oil + soluble resin	L + R 1:1		0.1104	0.0958	0.1135
Vinylcopolymer + Linseed oil + soluble resin	V + L + R 1:1:1		0.1120	0.1187	0.1430
Vinylcopolymer + soluble resin	V + R 1:1	02.02.92	0.0594	0.0721	0.0594
Linseed oil + soluble resin	L + R 1:1		0.1132	0.1124	0.1400
Vinylcopolymer + Linseed oil + soluble resin	V + L + R 1:1:1		0.0752	0.0873	0.0897
Vinylcopolymer + soluble resin	V + R 1:2	01.04.92	0.1061	0.1335	0.1390
Linseed oil + sluble resin	L + R 1:2		0.0792	0.0907	0.0807
Vinylcopolymer + Linsed oil	V + L 1:2		0.2730	0.2339	0.1759
Vinylcopolymer + soluble resin	V + R 1:2	05.05.92	0.1043	0.1173	0.1224
Linseed oil + soluble resin	L + R 1:2		0.1044	0.0802	0.0956
Vinylcopolymer + Linseed oil	V + L 1:2		0.3682	0.3065	0.2488
Vinylcopolymer + soluble resin	V + R 2:1	21.06.92	0.0751	0.0675	0.0618
Linseed oil + soluble resin	L + R 2:1		0.0640	0.0577	0.0726
Vinylcopolymer + Linseed oil	V + L 2:1		0.1102	0.1208	0.1228
Vinylcopolymer + soluble resin	V + R 2:1	28.07.92	0.0825	0.1140	0.0867
Linseed oil + soluble resin	L + R 2:1		0.1014	0.0976	0.0890
Vinylcopolymer + Linseed oil	V + L 2:1		0.1288	0.1391	0.1507

the media and examined for deterioration such as film peeling, lifting and colour change. The film was scraped from one side using a suitable remover and examined for all attached species of phytoplankton. At the same time, the sea water medium was analyzed for dissolved oxygen, nitrite, silicate, phosphate, alkalinity, salinity, dissolved organic matter, pH and temperature were measured. The phytoplankton and its dominant species were counted.

2.4 Analysis of Sea Water Samples

A surface water sample was collected monthly over the period September 1991–July 1992 from Alexandria Eastern Harbour from one station (Fig. 1) by means of a plastic

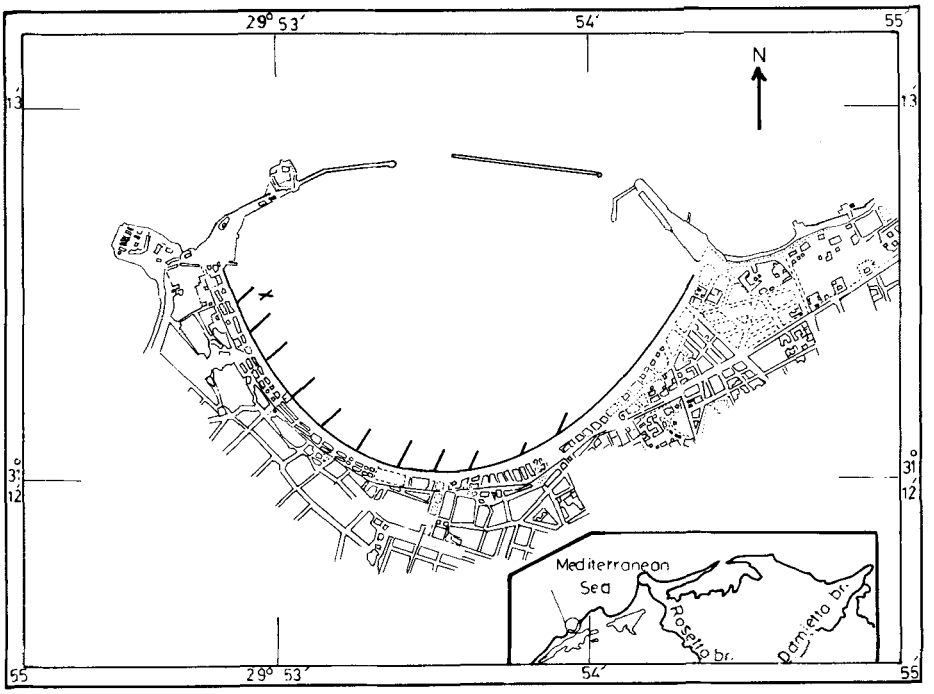

Figure 1 The Eastern Harbour, sampling station (x) and outfalls (l) br: branch.

Rutter water sampler. The sea water sample was analyzed immediately as well as the sea water media of the coated slides at the end of each inspection time. Dissolved organic matter was measured according to Korringa and Postma (1957). Dissolved oxygen, ammonia, silicate, phosphate, nitrite and alkalinity were measured according to the methods described by Grasshoff (1976). Salinity was calculated from electrical conductivity measured by indication salinometer, Beckman, Model R.S. 7BNO after making a temperature correction. Temperature and pH values were also recorded. Sea water samples were analyzed for phytoplankton standing crop using a sedimentation method (Ultermhöl, 1931). The different species were indentified and counted. Abundance is expressed in cells per litre.

3 RESULTS

Phytoplankton standing crop in the Eastern Harbour over the period September 1991–July 1992 was found to be in the range $0.03 \times 10^6 - 77 \times 10^6$ cells l^{-1} with dominant species *Skeletonema costatum* and *Prorocentrum triestinum* (Table II). This is a higher density than that previously recorded in the harbour (Sultan, 1975; Halim *et al.*, 1980; Zaghloul and Halim, 1990; Ragab, Pers. comm.).

Table III shows the variations of the chemical characteristics in the Eastern Harbour over the period September 1991 to July 1992. The temperature ranged between a minimum of 14.5°C in December and maximum of 26.8°C in August. The pH value at this station varied in the range 8.1 ± 0.48. The area is well oxygenated during most of

Table II Phytoplankton standing crop and its predominant species in Alexandria Eastern Harbour.

Period of investigation	*Standing crop (numbers)*	*Dominant spp.*
1972–1973	0.08×10^6–12.4×10^6	*Skeletonema costatum*
1977–1978	$0.001 \times 10^6 - 5 \times 10^6$	*Skeletonema costatum*
1986–1987	0.2×10^6–19×10^6	*Chaetoceros affinis* *Cyclotella meneghiniana* *Amphicrysis compressa* *Alexandrium minutum*
1990–1991	0.04×10^6–23.5×10^6	*Skeletonbema costatum* *Anabaena sp*
Sep. 1991–July 1992	0.03×10^6–77×10^6	*Skeletonema coastatum* *Prorocentrum triestinum*

the year. The concentration of phosphate found was between 0.00 and 24.8 $\mu g\ l^{-1}$. Ammonia concentration in this station is high and reaches a maximum of 206.6 $\mu g\ l^{-1}$ in November and a minimum during winter. The water samples showed a wide range of nitrite content ranging from 3.36–42.84 $\mu g\ l^{-1}$. Also, low organic matter (COD) was recorded (0.038–0.28 mg $O_2\ l^{-1}$).

A correlation matrix (Table IV) between the total numbers of phytoplankton and the measured physicochemical parameters, showed significant relationships between phytoplankton numbers and both dissolved ammonia-nitrogen and phosphate-phosphorus concentrations ($r = 0.59$ and 0.99 at $p > 0.05$, respectively). A negative correlation was found between the number of species and both phytoplankton numbers and phosphate-P concentration ($r = -0.74$ and -0.76 at $P > 0.05$) respectively.

On the other hand, correlation between the weight of each coating film and the phytoplankton numbers present in their media was also calculated. Table V shows that vinylcopolymer coating alone is correlated with numbers of the diatom *Thalassiosira decipiens*. The addition of a soluble resin material to the vinylcopolymer in a 1:1 ratio produces a coating that is negatively correlated with the numbers of the diatom *Skeletonema costatum* ($r = -0.56$ at $P > 0.05$) and positively correlated with the numbers of *Chaetoceros affinis* ($r = 0.65$ at $P > 0.05$). Both 1:2 and 2:1 ratios of vinylite and soluble resin have a significant correlation with total phytoplankton numbers. A coating with the latter ratio is also positively correlated with numbers of the diatom *Bellorochea malleus*. In contrast, linseed oil film coating and its formulations have no correlation with total phytoplankton numbers except as the L + R (2:1) ratio formulation. Linseed oil film coating is significantly correlated with both total dinoflagellates and *Thalossiosira decipiens*. Also, L + R 1:1 and 2:1 formulations are correlated with numbers most of the identified phytoplankton species (Table V). The polymeric coatings of both vinylite and linseed oil with 1:2 and 2:1 ratios are correlated with total phytoplankton standing crop although coatings containing either as a sole binder show no correlation. The coating with the 2:1 ratio is also correlated to the numbers of both *Bellorochea malleus* ($r = -0.93$ at $P > 0.05$) and *Skeletonema costatum* ($r = -0.72$

Table III Some physicochemical characteristics of sea water measured at the selected station in Alexandria Eastern Harbour

Date	*Temp.* °C	pH	*DO* ml O_2 l^{-1}	*Alk.* meq l^{-1}	*OM* mg O_2 l^{-1}	NO_2-*N*	NH_3-*N* $\mu g\ l^{-1}$	PO_4-*P*	SiO_2-*Si*	*S*‰
22.09.91	26.0	—	3.68	0.468	—	34.16	38.64	25.42	10.39	—
22.10.91	—	7.88	4.10	1.20	—	20.86	167.86	15.19	24.43	—
24.11.91	—	8.00	5.91	—	0.24	42.84	206.64	3.41	0.56	—
29.12.91	14.5	7.82	1.27	—	—	—	00.00	—	—	—
23.01.92	16.0	8.60	4.86	1.84	0.045	35.28	—	0.00	3.57	36.142
20.02.92	15.2	—	5.01	1.22	0.107	4.90	4.34	0.00	0.00	40.32
01.04.92	17.8	8.52	5.01	3.46	0.110	3.36	—	10.23	1.74	40.971
05.05.92	19.8	7.65	4.44	3.65	0.110	8.82	130.06	16.74	0.00	39.57
21.06.92	25.1	8.40	2.86	1.75	0.038	4.90	00.00	12.40	—	40.358
28.07.92	26.8	8.48	3.85	3.00	0.280	9.52	46.62	11.78	104.76	37.308

Table IV Correlation matrix between phytoplankton standing crop and some hydrographic characteristics.

No. of spp.	X_1	*Phytoplankton numbers/l* X_2	*Do* X_3	*pH* X_4	*Alk.* X_5	PO_4-P X_6	NO_2-*N* X_7	NH_3-*N* X_8	Sio_2-*Si* X_9
X_1	1								
X_2	−0.74	1							
X_3	−0.10	0.04	1						
X_4	−0.019	0.18	−0.67	1					
X_5	−0.46	0.39	0.35	−0.35	1				
X_6	−0.76	0.99	0.06	0.18	0.40	1			
X_7	0.62	0.31	0.07	0.25	−0.59	−0.37	1		
X_8	0.26	0.59	0.12	0.19	0.18	−0.56	0.17	1	
X_9	0.22	−0.12	−0.25	0.22	0.16	−0.13	−0.01	−0.96	1

Table V Correlation matrix between the weight of coating films and the phytoplankton numbers present in their media.

	Formulations											
Phytoplankton	*V*	*V* + *R* *1:1*	*V* + *R* *1:2*	*V* + *R* *2:1*	*L*	*L* + *R* *1:1*	*L* + *R* *1:2*	*L* + *R* *2:1*	*V* + *L* *1:1*	*V* + *L* *1:2*	*V* + *L* *2:1*	*V* + *L* + *R* *1:1:1*
Total phytoplankton	−0.15	0.72	0.73	−0.64	0.15	−0.49	−0.19	−0.60	−0.19	−0.73	−0.72	0.37
Skeletonema costatum	0.25	−0.57		−0.27	0.12	−0.02		−0.71	−0.19		−0.72	0.23
Thalassiosira decipiens	0.57				0.71				0.97			
Dinoflagellates	0.13		0.07		0.99		0.21			−0.03		
Nitzschia delicatissima		0.21				−0.96						0.38
Chaetoceros sp.		0.65				−0.99						−0.52
Bellorochea malleus				0.90				0.91			−0.93	
Asterionella japonica						−0.59						0.97

at $P > 0.05$). Coatings consisting of a 1:1 ratio of both binders (V + L) and also those including soluble resin (V + L + R) (1:1:1) have similar correlations to those for the coatings based on either, showing no correlation with total number of phytoplankton, but strong correlations with numbers of *Thalassiosira decipiens* and *Asterionella japonica* ($r = 0.97$ at $P > 0.05$ in both cases).

The total numbers of phytoplankton as well as the numbers of each predominant species found on the coated substrates or their presence in the media have been counted for each formulation, Table VI. The total numbers of phytoplankton, mainly filamentous forms, found on the substrates are greatly affected by the coatings of most formulations. Most are changed from dominant (+ + +) and frequent (+ +) on the blank slides to rare (+) or completely absent on the treated slides. It is also clear that linseed oil based coatings and its formulations with soluble resin material are more effective towards epiphyte (fouling) phytoplankton than vinylcopolymer formulations.

No epiphytes were detected on the substrates coated with linseed oil or its formulations with soluble resin in 1:2 or 2:1 ratios over the whole immersion period in November, where a small number of filamentous forms appeared on linseed oil coated slides during the seventh and tenth days of immersion.

DISCUSSION

All prepared coatings have an effect on the total numbers of phytoplankton and some of its dominant species present in their media. They decrease or increase in their numbers according to the change in environmental conditions, the date of immersion and the coating composition. Also, the coating effectiveness is affected by the numbers of phytoplankton which adhere to the substrates and the presence of ciliates in their media.

Vinylcopolymer Coatings

A coating based on vinylcopolymer only was tested over four months (from Sept–Dec. 1991). The dominant species appearing during this period are *Skeletonema costatum*, dinoflagellates and *Thalassiosira decipiens*.

At day 14, the numbers of the phytoplankton in the media of the treated slides are either no different from the blank, as in December and January, or increased more than two-fold as in September. In this month and at day 14, there is a pronounced increase in NH_3-N concentration (185.5 $\mu g\ l^{-1}$). During October, phytoplankton numbers decreased at the same inspection time; this was accompanied by a decrease in dissolved organic matter concentration to reach 0.117 mg $O_2\ l^{-1}$ in comparison with 0.254 mg $O_2\ l^{-1}$ in the blank. A similar effect of the coating was recorded with *Skeletonema* and total dinoflagellates. Except during December, the coating showed 87.2% and 65.7% inhibition against *Skeletonema costatum* and *Thalassiosira decipiens*, respectively. During December some gasoline odour was detected in water samples and this contamination affected the water characteristics. Dissolved oxygen was reduced to 0.74 ml $O_2\ l^{-1}$, while some other components such as alkalinity, organic matter,

nitrite-N, phosphate-P and silicate-Si could not be detected due to the turbidity of the water sample. At the seventh and tenth days of immersion, the coating had both neither positive nor negative effect towards phytoplankton numbers and its dominant species. It was noticed that when the inhibition of vinylcopolymer coating against phytoplankton was high at the first inspection time (7 days), a lower effect of the coating was observed at day 14, and *vice versa*. Generally there were no ciliates (Protozoa) detected with the vinylcopolymer coating.

Linseed Oil Coating

This coating was tested over three months (October, November and December). It has a greater inhibiting effect on total phytoplankton and *Skeletonema* species than vinyl copolymer coatings over the whole inspection time, except in November when the numbers of both greatly exceeded that in the medium of vinyl copolymer coating at the seventh and tenth days of immersion; this was accompanied by higher suspended organic matter concentration, Table VII. Also, at these times (7 and 10 days) there were few epiphytes found on the substrate, and they were completely absent from the rest of the slides. Generally a sharp decrease in dissolved oxygen and NO_2-N concentrations was recorded with linseed oil coating, ranging between 0.32–3.59 ml $O_2\,l^{-1}$ and 0.00–42.56 $\mu g\,l^{-1}$ in comparison with 0.21–5.91 ml $O_2\,l^{-1}$ and 0.76–190.26 $\mu g\,l^{-1}$ with medium of vinyl coating. The number of ciliates changed from rare in the blank to either dominant or frequent in the media of linseed oil coatings. So, the sharp decrease in dissolved oxygen and nitrite-nitrogen concentrations in the sea water medium of the slide coated with linseed oil as well as the increase in the number of ciliates may explain the decrease in phytoplankton numbers with this coating.

Vinyl Copolymer and Linseed Oil Coatings

The three formulations between the two binder materials with ratios 1:1, 1:2 and 2:1 have different effects on the total numbers of phytoplankton and its species. V + L (1:1 ratio) coating was tested in November and December. It showed higher inhibitory effect towards phytoplankton, *Skeletonema* and *Thalassiosira* species than the individual binder coatings which were tested at the same time. Except in November, and at the last inspection time (14 days), both numbers of *Skeletonema* species and total phytoplankton exceed their numbers in the medium of linseed coating. The increase in their numbers was accompanied by increased NO_2-N concentration compared with that recorded with the other media.

The effect of the two formulations with the ratios 1:2 and 2:1 on phytoplankton and its species is based on the month of inspection. Generally, they both showed a weaker effect than with the 1:1 ratio coating. No epiphytes appeared on the slide coated with 1:2 ratio formulations, while with the 2:1 ratio only a rare number was observed. 1:2 ratio formulation showed some inhibition against phytoplankton, and of total dinoflagellate species (present in April and May) at day seven of immersion, when their numbers increased to exceed their analogue in the blank. Except in May, its effect against phytoplankton standing crop extended at all inspection dates due to the decrease in NO_2-N and NH_3-N concentrations. The number of protozoa in these

Table VI Number of total phytoplankton and its dominant species (cells l^{-1}) after 7, 10 and 14 days of immersion and percent (in brackets) with respect to the blank.

Immersion	*Phytoplankton species*	*C*	*B*			
time			*7*	*10*	*14*	*7*
22.09.91	Phytoplankton epiphyte		+	++	++	+
	Total phytoplankton	4819	4604	477	139	1555 (33.8)
	Skeletonema costatum	4443	4500	440	117	1500 (33.3)
22.10.91		*C*		*B*		
	Phytoplankton epiphyte		+		++	+
	Taotal phytoplankton	3358	702		1049	1662 (236.8)
	Skeletonema costatum	2700	552		840	1455 (263.6)
	Dinoflagellate	379	48		105	47 (97.9)
24.11.91		*C*		*B*		
	Phytoplankton epiphyte		+++	+++	+++	+++
	Total phytoplankton	3833	6260	492	167	628 (10.03)
	Skeletonema costatum	3.6×10^6	6030	396	125	550 (9.12)
29.12.91		*C*		*B*		
	Phytoplankton epiphyte		−	+	+	−
	Total phytoplankton	34	447	1221	799	330 (73.8)
	Skeletonema costatum	11	380	1050	720	285 (73.1)
	Thalassiosira decipiens	2	34	35	70	4 (11.8)
23.01.92		*C*		*B*		
	Phytoplankton epiphyte		++	+++	+++	+
	Total phytoplankton	327	2210	446	249	650 (29.4)
	Nitzschia delicatissima	175	990	42	54	110 (11.1)
	Chaetoceros sp. affinis	105	1008	234	124	230 (22.8)
20.02.92		*C*		*B*		
	Phytoplankton epiphyte		++	+++	++	+
	Total phytoplankton	1992	10152	9634	3025	3020 (29.7)
	Skeletonema costatum	738	4086	7650	1590	2166 (53.0)
	Asterionella japonica	549	5940	1680	1555	690 (11.6)

V							
10	*14*						
+	+						
108	318						
(22.6)	(228.8)						
35	290						
(7.14)	(147.9)						
V			*L*				
	+	−		−			
	491	318		116			
	(46.8)						
	432	192		34			
	(51.4)	(34.8)		(4.1)			
	18	37		48			
	(17.14)	(77.1)		(45.7)			
V			*L*			*V + L 1:1*	
+ +	+ + +	+	+	−	+	+	+ +
483	168	4340	1432	130	99	139	143
(98.2)	(100.6)	(69.3)	(291.1)	(77.85)	(1.6)	(28.3)	(85.6)
457	138	4.02×10^3	1380	42	21	101	63
(115.4)	(104)	(66.7)	(348.5)	(33.6)	(0.4)	(25.5)	(50.4)
V			*L*			*V + L 1:1*	
−	−	−	−	−	−	−	+
959	799	74	140	123	36	158	3
(78.5)	(100)	(10.6)	(11.5)	(15.39)	(8.1)	(12.94)	(0.38)
735	92	20	50	20	15	73	−
(70)	(12.8)	(5.13)	(4.76)	(2.8)	(3.85)	(6.95)	−
51	24	39	9	6	4	8	−
(145.7)	(34.3)	(114.7)	(25.7)	(8.6)	(11.76)	(22.9)	−
V + R 1:1			*L + R 1:1*			*V + L + L 1:1:1*	
+	+	−	−	+	−	−	−
990	243	1561	1108	125	1118	917	180
(221.9)	(97.9)	(70.6)	(248.4)	(50.2)	(2.42)	(205.6)	(72.3)
213	12	420	44	11	24	29	25
(507.1)	(22.2)	(42.4)	(104.8)	(50.2)	(2.42)	(691)	(46.3)
339	100	960	900	81	864	804	112
(140.6)	(80.6)	(95.2)	(384.6)	(65.3)	(85.7)	(343.6)	(90.3)
V + R 1:1			*L + R 1:1*			*V + L + R 1:1*	
−	−	−	−	−	−	−	−
1916	761	3542	929	2323	2674	2550	2399
(19.9)	(25.2)	(35.4)	(9.64)	(76.8)	(26.3)	(26.5)	(79.3)
1320	320	1710	465	1950	1875	1680	1230
(17.3)	(25.2)	(41.9)	(16.08)	(122.6)	(45.9)	(26.5)	(77.4)
495	300	1740	375	330	735	810	1110
(29.5)	(19.3)	(29.3)	(22.2)	(21.2)	(12.4)	(48.2)	(71.4)

1.04.91		*C*		*B*		
	Phytoplankton epiphyte		+ +	+ +	+	−
	Total phytoplankton	2680	7852	503	54	467 (5.9)
	Dinoflagellate	2655	1447	364	12	97 (6.7)
5.05.92		*C*		*B*		
	Phytoplankton epiphyte		+ + +	+ + +	+ + +	+
	Total phytoplankton	624	1332	1675	447	419 (31.4)
	Dinoflagellate		102	3	8	42 (41.2)
21.06.92		*C*		*B*		
	Phytoplankton epiphyte		+ +	+ +	+ +	+
	Total phytoplankton	390	20	37	16	57 (285)
	Bellorochea mellus	234	2	−	−	1 (50)
28.07.92		*C*		*B*		
	Phytoplankton epiphyte		+ +	+	+ +	+
	Total phytoplankton	2480	266	1129	383	183 (68.8)
	Skeltonoma costatum	3375	225	950	285	105 (46.7)

C = Contorol, sea water medium without slide immersion;
B = Blank, sea water medium with untreated slide
V = Sea water medium having slides coated with vinylcopolymer binder only.
+ = rare, + + = Frequent, + + + = Dominant (Filamentous);

media formulations changed from frequent to rare in April and from frequent to dominant in May and then decreased again till the last time of inspection.

The 2:1 ratio formulation had no effect on total phytoplankton numbers at the first seven days of inspection. Its greatest effect appeared on day 10, when the numbers increased again. *Bellorochea* and *Skeletonema* species appeared in June and July where the effect of this formulation reached its maximum at days 14 and 10. The presence of ciliates in this medium is rare. In June, at day 14, free-living nematodes appeared. Both months differed in salinity which was higher in June than in July by about 3%

Vinyl copolymer, Linseed Oil and Soluble Resin Coatings

The formulations V + R, L + R and V + L + R with 1:1 ratios were tested in January and February. The predominant phytoplankton species in both months differed (Table VI). No epiphytes were detected on slides coated with the latter two coatings, but their number was rare on V + R coated surface. The three formulations were significantly correlated with most of the identified species (Table V).

V + R 1:2			*L + R 1:2*			*V + L 1:2*	
–	–	–	–	–	–	–	–
254	29	630	189	202	748	1789	172
(50.5)	(53.7)	(8.02)	(37.6)	(374.1)	(9.5)	(355.7)	(318.5)
24	8	86	71	43	699	31.8	83
(6.6)	(66.7)	(5.9)	(19.5)	(358.3)	(48.3)	(87.4)	691.7)
V + R 1:2			*L + R 1:2*			*V + L 1:2*	
+	+	–	–	–	–	–	–
131	79	183	47	59	162	216	113
(7.8)	(17.7)	(3.7)	(2.8)	(13.2)	(12.2)	(12.8)	(25.3)
6	72	21	9	7	24	59	86
(200)	(900)	(20.6)	(300)	(87.5)	(23.5)	(1966.7)	(1075)
V + R 2:1			*L + R 2:1*			*V + L 2:1*	
+	+	–	–	–	+	+	+
29	79	210	95	15	175	29	60
(78.4)	(493.8)	(1050)	(256.8)	(93.8)	(875)	(78.4)	(375)
–	–	–	–	4	8	2	–
				(400)	(400)	(200)	
V + R 2:1			*L + R 2:1*			*V + L 2:1*	
+	+	–	–	–	+	+	+
416	235	147	219	276	367	426	358
(36.6)	(61.4)	(55.3)	(19.4)	(72.1)	(138)	(37.7)	(93.5)
183	10	95	112	84	175	180	92
(19.3)	(3.5)	(20)	(11.8)	(29.5)	(77.8)	(18.9)	(32.3)

During January, the three formulations had nearly similar trends of their effectiveness against total phytoplankton and species presence. At day 7 both V + R and V + L + R formulations showed a higher inhibitive potential than at day 14 against the total number of phytoplankton, *Nitzchia delicatissima* and *Chaetoceros affinis*, but with L + R formulation, a lower potential (i.e. lower percent numbers of total phytoplankton and species with respect to the blank) was recorded at day 14 than at day7. On the other hand, the increase and decrease in the total number of phytoplankton and the two species in the media of the treated slides followed changes in alkalinity concentration (Table VII).

In February, the three formulations showed their highest inhibitory effect against the total phytoplankton and *Skeletonema costatum* at day 10. This effect was accompained by increase in alkalinity.

The formulations V + R and L + R with 1:2 and 2:1 ratios were tested from April till July. No epiphytes formed on the L + R coating surface, but their number was rare on V + R film coatings. The formulations V + R and L + R in 1:2 ratio showed nearly the same trend of their effectiveness in April and May against both total phytoplankton

Table VII List of physicochemical parameters measured after 7, 10 and 14 days in the medium of the blank and the media of the coated slides.

Immersion time	Formulation*	pH			DO* (ml O_2 l^{-1})			Alk. (meq l^{-1})			OM**
		7	10	14	7	10	14	7	10	14	7
22.9.91	B	7.99	7.97	–	4.82	3.48	5.29	1.31	1.39	1.40	15.96
	V	7.95	7.90	–	5.10	5.91	4.96	1.14	1.40	1.26	17.50
22.10.91	B	7.98	7.69	7.69	5.81	5.91	5.91	1.59	1.31	1.40	52.36
	V	8.00	7.85	7.73	6.97	6.44	5.91	1.59	1.31	1.40	31.50
	L	7.50	7.38	7.32	1.16	2.96	3.59	1.22	1.12	1.12	2.24
24.11.91	B	7.96	7.78	7.74	5.39	7.39	6.03	–	1.25	1.17	72.80
	V	7.74	7.53	7.64	4.33	5.39	5.91	–	1.17	1.09	49.28
	L	7.33	7.11	7.22	1.056	10.56	2.01	–	1.00	1.09	1.82
	V + L 1:1	7.44	7.03	7.25	1.37	1.90	2.22	–	1.00	1.17	4.20
29.12.91	B	7.49	7.54	7.29	0.42	0.63	0.26	1.505	1.44	1.421	6.31
	V	7.38	7.54	7.22	0.21	0.63	0.74	1.338	1.17	1.421	21.98
	L	7.40	7.11	6.89	0.32	0.32	0.32	1.254	1.254	1.087	–
	V + L 1:1	7.70	7.11	7.00	0.32	0.42	0.37	1.170	1.505	1.421	–
03.01.92	B	–	8.3	8.14	5.39	4.75	4.44	1.169	1.253	1.253	27.66
	V + R 1:1	–	8.15	8.12	4.12	4.75	4.44	1.253	1.587	1.169	28.42
	L + R 1:1	–	7.91	7.63	0.84	0.32	0.74	1.169	1.83	1.33	0.00
	V + L + R 1:1:1	–	7.78	7.60	0.32	0.11	0.48	1.169	1.75	1.169	0.00
20.02.92	B	8.10	8.15	7.73	4.53	5.19	4.72	1.22	1.66	1.57	3.42
	V + R 1:1	7.85	8.00	7.83	3.31	3.97	3.97	1.31	1.61	1.76	–
	L + R 1:1	8.11	7.69	7.44	2.55	1.98	2.46	1.309	1.53	1.53	–
	V + L + R 1:1:1				5.10	1.98	2.08	1.31	1.49	1.04	6.44
01.04.92	B	7.97	7.56	8.05	4.34	4.25	4.16	3.83	3.55	3.46	5.68
	V + R 1:2	7.61	7.75	7.59	1.13	2.55	1.23	3.647	3.46	3.553	–
	L + R 1:2	7.60	7.57	7.68	1.79	1.42	2.46	3.553	3.366	3.366	0.00
	V + L 1:2	7.45	7.98	7.61	1.32	1.51	2.27	3.55	3.37	3.179	0.00
05.05.92	B	8.43	8.45	8.23	4.34	3.25	3.98	3.36	3.27	3.54	10.61
	V + R 2:1	8.13	8.22	8.10	1.61	1.46	2.13	3.71	3.27	3.98	–
	L + R 2:1	7.93	8.08	8.07	0.66	1.33	2.79	3.10	3.19	3.10	0.00
	V + L 1:2	7.87	7.93	8.00	1.61	0.46	1.86	3.10	3.45	3.27	0.00
21.06.92	B	8.33	8.50	8.52	3.39	4.65	4.25	1.62	1.91	1.787	18.19
	V + R 2:1	7.87	8.44	8.49	1.00	4.12	4.05	1.40	1.70	1.617	3.04
	L + R 2:1	8.12	8.18	8.25	2.79	2.72	2.86	1.62	1.87	1.787	0.38
	V + L 2:1	8.31	8.28	8.33	3.92	3.45	3.59	1.57	1.57	1.617	23.49
28.7.92	B	8.25	8.10	8.16	3.84	4.23	3.10	3.04	3.12	3.12	43.96
	V + R 2:1	8.12	7.92	7.72	3.18	2.54	2.92	3.20	3.04	3.12	32.97
	L + R 2:1	7.81	7.57	7.46	1.43	1.41	1.79	3.04	3.20	3.20	0.00
	V + L 2:1	7.93	7.75	7.45	2.30	1.50	2.07	3.12	3.04	3.04	0.00

* DO = Dissolved Oxygen
**OM = Dissolved organic Matter.

numbers and total dinoflagellates. Their maximum effect was recorded at day 7 of inspection, but in May, they reached their highest potential at the day 10 against phytoplankton only. As observed above, the decrease in phytoplankton numbers and its predominant species is accompanied by an increase in alkalinity concentration with a value ranging between 3.65-3.56 meq l^{-1} in April at day 7, in comparison to 3.55–3.37 meq l^{-1} during other times of inspection. During June and July, most of the total numbers of phytoplankton and the two predominant species in the media of the polymeric coatings V + R and L + R in 2:1 ratio reached their lowest number at day 10 of inspection with increase in alkalinity. The number of ciliates in the treated medium of

NO_2-N			NH_3-N			PO_4-P			SiO_2-Si			OM**	
$\mu g\,l^{-1}$			$\mu g\,l^{-1}$			$\mu g\,l^{-1}$			$\mu g\,l^{-1}$			$mg\,O_2\,l^{-1}$	
10	*14*	*7*	*10*	*14*	*7*	*10*	*14*	*7*	*10*	*14*	*7*	*10*	*14*
61.04	16.66	276.8	215.46	197.82	5.05	5.05	18.54	6.97	8.71	5.22	0.027	–	–
14.84	20.16	248.78	116.76	185.50	8.43	6.73	8.43	3.48	8.71	0.17	0.107	0.068	0.027
192.08	84.84	167.86	–	196.00	1.67	–	–	43.53	10.45	0.00	0.277	0.268	0.254
114.80	190.26	0.00	–	31.64	1.67	–	–	19.15	–	–	0.361	0.134	0.107
0.00	1.89	169.68	–	76.44	1.67	–	–	29.60	5.22	0.00	0.214	0.602	0.615
71.26		15.82	–	–	5.05	–	–	5.22	–	–	0.539	0.209	0.209
52.36		–	–	–	6.73	–	–	5.22	–	–	0.239	0.299	0.194
42.56		–	–	–	10.23	–	–	5.22	–	–	0.883	0.972	0.628
28.84	4	–	–	–	6.94	–	–	3.48	–	–	0.703	0.763	0.688
2.65	10.234	–	–	–	28.64	102.8	13.49	20.90	6.97	8.71	–	–	–
0.76	–	–	–	–	0.00	0.00	–	19.15	3.48	–	–	–	–
0.76	–	–	–	–	–	52.24	–	–	10.45	–	–	–	–
1.51	–	–	–	–	–	–	–	–	–	–	–	–	–
24.25	74.65	0.00	–	–	28.64	102.80	13.49	1.74	3.48	–	–	–	–
27.29	32.59	–	–	–	0.00	0.00	–	1.74	1.74	–	–	–	–
–	–	–	–	–	–	52.24	–	–	34.83	–	–	–	–
–	–	–	–	–	–	5.05	–	33.09	10.45	–	–	–	–
7.95	14.42	34.30	7.91	12.31	5.05	–	–	–	–	–	0.214	0.094	0.067
13.76	15.27	37.80	9.55	9.55	–	–	–	–	–	–	0.655	0.107	0.120
–	–	21.14	9.55	–	–	–	–	–	–	–	0.589	0.562	0.575
–	–	0.00	–	–	4.96	–	–	–	–	–	0.161	0.548	0.655
5.68	9.86	–	–	2.02	0.00	–	276.37	0.00	–	–	0.04	0.04	0.054
–	–	–	–	1.76	0.00	–	134.82	0.00	–	–	0.348	0.455	0.415
–	0.76	0.00	–	6.85	0.00	–	–	0.00	–	–	0.535	0.562	0.535
0.00	0.00	–	–	9.55	0.00	–	0.00	0.00	–	–	0.548	0.562	0.682
15.54	1.89	113.4	228.62	51.94	11.81	35.34	0.00	–	0.00	–	0.040	0.04	0.054
0.00	–	–	–	0.00	13.58	6.73	5.05	–	0.00	–	0.348	0.455	0.415
0.00	0.00	0.00	70.28	0.00	6.73	13.49	6.73	–	0.00	–	0.535	0.562	0.535
0.00	0.00	0.00	14.98	0.00	10.11	10.11	0.00	–	0.00	–	0.548	0.562	0.682
81.86	121.65	–	27.30	141.54	30.32	21.92	32.02	–	–	–	0.113	0.103	0.122
48.89	62.44	–	43.12	14.07	45.57	16.86	10.11	–	–	–	0.358	0.113	0.132
0.38	0.00	–	0.88	6.16	21.92	1.67	5.05	–	–	–	0.160	0.461	0.517
0.38	0.00	–	3.51	8.68	85.87	6.73	3.38	–	–	–	0.047	0.160	0.160
101.93	56.56	–	203.98	113.40	15.16	64.05	488.56	–	–	–	0.217	0.147	0.280
19.71	378.95	–	121.38	104.58	11.81	20.21	555.83	–	–	–	0.217	0.160	0.508
1.89	1.89	–	0.00	1.76	15.44	3.38	10.11	–	–	–	0.59	0.44	0.70
1.89	2.27	6.85	3.04	7.57	15.16	6.73	16.77	–	–	–	0.388	0.373	0.480

V + R (2:1 ratio) was rare, but changed from rare to dominant in L + R (2:1 ratio) formulation.

CONCLUSIONS

There is no significant correlation between the weight of films of either vinylcopolymer and linseed oil coatings and the total numbers of phytoplankton present in their sea water media. Their formulations together with 1:2 and 2:1 ratios as well as the

formulation of each with resin material (V + R 2:1, V + R 1:2 and L + R 2:1) are significantly correlated with phytoplankton numbers. Also, most of the coatings with mixed binders of vinyl resin, linseed oil and soluble resin are significantly correlated with numbers of most identified phytoplankton species.

The negative correlation between the number of species and phosphate concentration and the positive one with phytoplankton standing crop indicates eutrophication in the Eastern Harbour.

The effect of the coatings on phytoplankton numbers is related to some chemical variables such as nitrite, ammonia, organic matter and alkalinity.

Dissolved oxygen, nitrite-nitrogen and the number of phytoplankton decrease in the media of linseed oil coatings, while the number of ciliates increases more in their media than in the blank.

There is no relation between the number of epiphytes on the coated substrates and the change in phytoplankton numbers present in their media.

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