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INTRODUCTION

Vessel antifouling paints constitute a potentially signficant source of certain trace contaminants to coastal marine waters. For example, copper, mercury, and lead have been used extensively in bottom paints or primers, and relatively high concentrations of polychlorinated biphenyls (PCB) also have been found in such materials (Barry 1972; Young et al. 1973; McClure, personal communication*). Because of the extensive use of recreational, commercial, and naval vessels off southern California, the Coastal Water Project conducted a study of the application of antifouling paints to boats in marinas and harbors along this coast. Samples of the principal brands of paints used were obtained and analyzed for PCB. In addition, when possible, copper content was obtained from the paint can labels. The results of this survey have been incorporated into estimates of annual mass emission rates (or their upper limits) for these potential pollutants, and the values have been compared to past estimates for two other sources.

PROCEDURES AND RESULTS

Field Surveys

The southern California coastline has 14 major recreational marinas between Santa Barbara and the U.S./Mexico border (Figure 1); in addition, there are major harbors at Los Angeles and San Diego that contain almost all of the commercial and naval drydock facilities in the region. During 1971, the number of small craft then maintained in each marina was obtained from the appropriate harbor master (Table 1). This inventory was followed by a preliminary investigation into the usage of antifouling paints and other vessel-related materials in Marina del Rey, the second largest marina in southern California (Southern California Coastal Water Research Project 1973). During 1973, we conducted detailed investigations into antifouling paint usage at four marinas--Ventura Harbor and Oxnard-Channel Islands Harbor (Ventura County), Marina del Rey (Los Angeles County), and Newport Bay (Orange County). These anchorages accommodate more than half of the marine recreational craft moored in southern California.

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* Dr. Vance McClure, National Marine Fisheries Service, Tiburon, Ca.

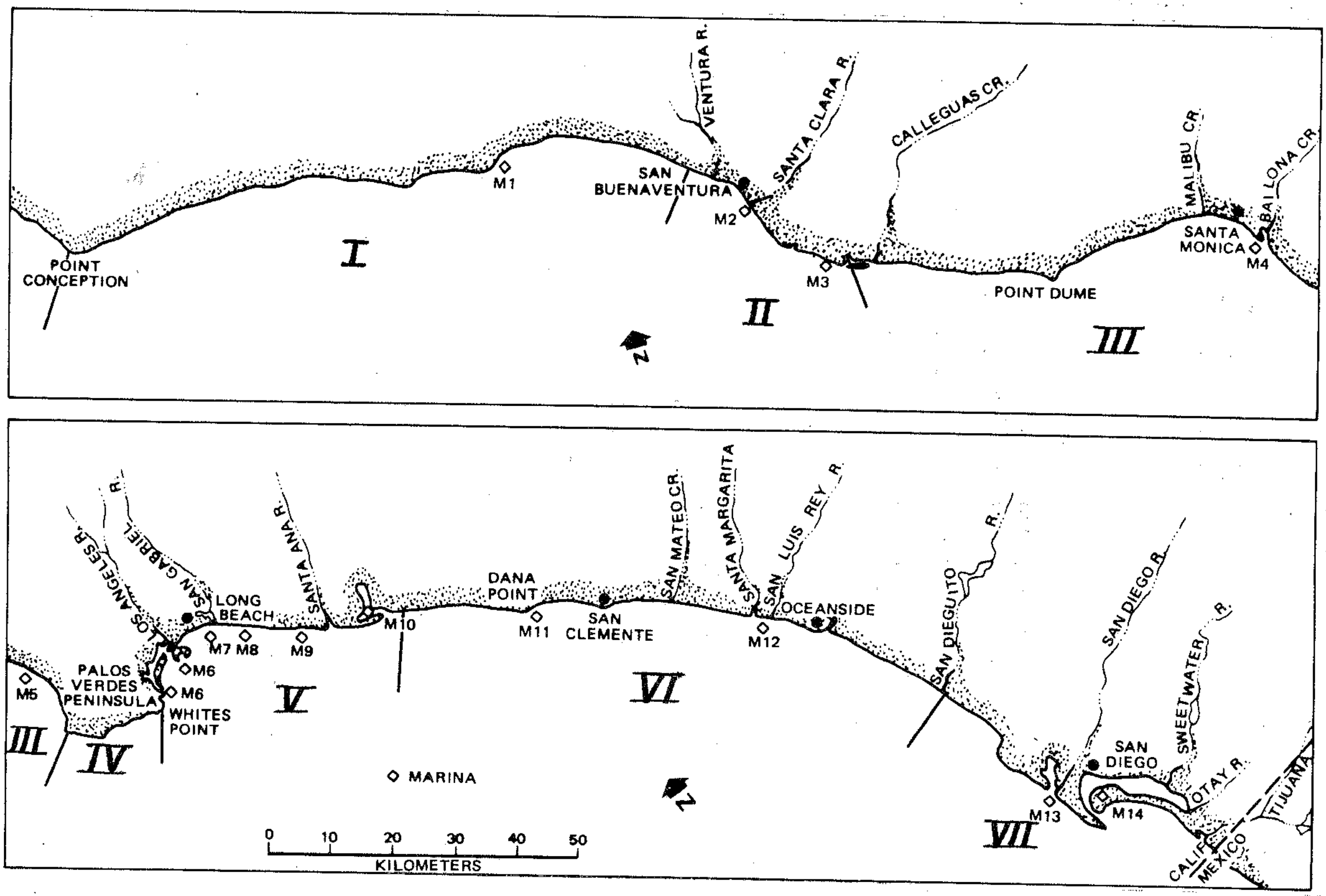

Figure 1. Southern California Marinas

Table 1

Number of Boats Harbored in
Southern California Marinas, 1971.

Ref. No.[a]	Marina	No. of Boats[b]
M1	Santa Barbara Harbor	750
M2	Ventura Harbor	930
M3	Oxnard-Channel Islands Harbor	930[c]
M4	Los Angeles-Marina del Rey	5,500[d]
M5	Redondo Beach-King Harbor Marina	1,400
M6	San Pedro Bay-Los Angeles Harbor	3,400
M7	San Pedro Bay-Long Beach Harbor	2,530
M8	San Pedro Bay-Long Beach Marina	2,300
M9	Huntington Beach-Huntington Harbor	3,200
M10	Newport Bay-Newport Beach Harbor	8,000[e]
M11	Dana Point Harbor	550
M12	Oceanside Harbor	550
M13	San Diego-Mission Bay	1,500
M14	San Diego Bay	3,320
	TOTAL	34,860

a. Key to location on Figure 1
b. Includes only 16- to 65-ft boats corresponding to U.S. Coast Guard Classes 1, 2, and 3. Boats smaller than 16 ft, which are U.S. Coast Guard Class A, are not included in this inventory.
c. 1973 estimate: 980 boats.
d. 1973 estimate: 6,000 boats.
e. 1973 estimate: 8,600 boats.

Information on boat size and type was generally not available; however, we located relatively detailed data on one recreational craft anchorage--Newport Bay.* This bay, which is located in approximately the middle of the Project's coastal study region, harbors almost 25 percent of the total number of small craft anchored in southern California; thus, we felt it would be reasonably representative of the other marinas of interest. Table 2 gives the results of an inventory of the numbers of power, sail, and hand-powered craft in several length classes moored in the Bay during winter 1971. Table 3 presents information on annual counts of craft of a number of different types anchored there between 1962 and 1971.

We used two methods to obtain estimates of the amounts of antifouling paint used. The first was to quantify directly the number of gallons of all major brands applied or sold annually in a marina area. The second was to obtain estimates of the average number of gallons of antifouling paint applied per boat and the number of boats painted annually in the area. In addition, data on the percentage use of each of the major brands was sought. Such information was obtained by visiting all of the boat "haul-out" yards in the marina under study and all of the retail paint and hardware stores in the vicinity of the marina. We obtained samples of paints currently in use, and also collected paint scrapings at several of the yards.

During 1973, our detailed survey efforts were first directed to Marina del Rey. Only two haul-out yards and four retail suppliers of antifouling paints were located in the vicinity. Information obtained on principal brands used and estimated application rates is summarized in Table 4.

Following the collection of the information summarized in Table 4, we attempted to evaluate the completeness of the survey of antifouling paint usage on Marina del Rey craft. Paint retailers' estimates of the number of gallons applied per boat (averaging approximately 30 ft (10 m) in length) ranged from 0.5 to 1.5.** Taking an average figure of 1 gal. per boat, and assuming that sales by Retail Store No. 4 (Table 4) were similar to those of the other three local retailers (averaging about 100 gal./yr), the painting of approximately 400 boats is accounted for by retail paint sales. This compares to approximately 4,100 boats painted annually by the two boat yards. In addition, another 300 boats that did not require antifouling paint were inventoried in dry storage. As the

* Larry Miller, Newport Beach Chamber of Commerce, personal communication.

** Estimates from the haul-out yards were somewhat higher, averaging about 1.5 gal./boat.

Table 2

Estimated Numbers of Power, Sail, and Hand-powered Boats in Five Length Classes - Newport Bay, Winter 1971.

Length	Power	Sail	Hand-Powered	Total
Under 20 ft	2,000	2,060	1,040	5,100
20-29 ft	1,200	980	-	2,180
30-39 ft	730	430	-	1,160
40-49 ft	360	120	-	480
Over 50 ft	150	70	-	220
TOTAL	4,440	3,660	1,040	9,140

average reported interval between paintings was 12 months, approximately 4,800 (or 80 percent) of the estimated 6,000 craft maintained at Marina del Rey were accounted for in the survey. We do not presently know how much of the remainder is due to unattended craft, to craft painted elsewhere or at a reduced frequency, or to inaccuracies in the usage estimates. However, it does appear that most of the paint applied to small craft anchored in Marina del Rey was accounted for in this survey.

A corresponding approach at the other marinas studied was not possible because our surveys revealed that some of the haul-out yards obtained their paints from local retail stores. However, in light of the fact that about 90 percent of the (accountable) antifouling paint used on Marina del Rey craft was applied by local boat yards, we have assumed that this is the predominant source of antifouling paints utilized on small craft in the marinas. Results on bottom paint usage for Newport Bay and Ventura and Oxnard Harbors are presented in Tables 5 and 6.

To obtain estimates of antifouling paints used in southern California on commercial and naval vessels, we visited most of the major drydock facilities in Los Angeles-Long Beach Harbor and San Diego Harbor. Estimates of the quantities and types of major paints applied annually at these drydocks was obtained (Tables 7 and 8). Samples of these paints also were collected and analyzed for PCB.

<u>Laboratory Technique</u>

<u>Wet Paint Extraction Methods</u>. Most samples were extracted using a separatory funnel. A measured volume of the wet paint sample was pipetted into a 500-ml separatory funnel containing 100 ml of 15 percent diethyl ether in hexane (by volume). If the paint

Table 3

Annual Inventory of Recreational Craft
in Newport Bay 1960-71.

	1971	1970	1969	1968	1967	1966	1965	1964	1963	1962	1961	1960
Cabin Cruisers	2,036	2,0181	2,076	2,029	1,966							
Motor Boats, Z-drives	790	771	642	746	682	2,743	2,462	2,462	2,7051	2,522		
Sailboats boats	3,703	3,562	3,308	3,129	3,129	3,055	2,585	2,266	2,208	2,119		
Out-boards	1,455	1,461	1,276	1,400	1,254	1,141	1,207	1,098	1,005	1,005		
Rowboats	964	804	738	903		969	895	825	864	1,047		
Canoes, Paddle Boards, Outriggers	58	54	38	47	27	20	34	20	21			
Kayaks, Pedaloes	41	82										
Dredges, Barges, Tugs	24	27	27	8	1	2			1			
House-boats	4	4	2				2					
Steam-boats	2	2	5	5								
Rafts, Floats	7	2	4									
Hull		2	1	1								
Rescue, Fire	6											
TOTAL	9,090	8,789	8,117	8,268	7,059	7,930	7,185	6,671	6,804	6,693	6,242	6,136

Table 4

Estimated Use of Antifouling
Paints at Marina del Rey, 1973.

Supplier	Boats/ Year		Average Gal./Boat		Gal./ Year	Brand	Est. % of Total
Boatyard No. 1	3,000	x	1.5	=	4,500	Brolite Z-Spar Woolsey	50 50
Boatyard No. 2	1,100	x	1.5	=	1,650	Brolite Z-Spar Woolsey	50 50
Paint Retailer No. 1	100*		1		100	Brolite Z-Spar Woolsey	- -
Paint Retailer No. 2	50*		1		50	Brolite Z-Spar Mariner's	95 5
Paint Retailer No. 3	150*		1		150	Brolite Z-Spar International	75 25
Paint Retailer No. 4	100*		-		100**	Brolite Z-Spar Woolsey	- -
TOTAL	4,500				6,550		

*Boats per year equals gallons per year divided by average gallons per boat.
**No quantitative information released; value assumed from data for Retailers 1 through 3.

seemed to disperse easily when dropped into the ether-hexane mixture, the separatory funnel method of extraction was employed. On the other hand, if the wet paint sample formed a seemingly nonpermeable drop or plastic-like string, the separatory funnel method was not used, and the samples were extracted using the Soxhlet method.

Separatory Funnel Method. The separatory funnel was shaken for a period of 2 minutes with the ether-hexane mixture and the sample. The sample was allowed to settle to the bottom of the separatory funnel, and the extract was carefully decanted into a round-bottomed flask. Next, 100 ml of 6 percent diethyl ether in hexane was added to the 500-ml separatory funnel containing the sample and shaken for a period of 2 minutes. Again the extract was carefully decanted into the round-bottomed flask. The paint was shaken again with 100 ml of hexane, and the extract was again added to the round-bottomed flask. The sample was reduced in a Rotovapor to a volume suitable for a Florisil cleanup.

Table 5.

Estimated Use of Antifouling Paints at Newport Bay, 1973.

Supplier	Boats per Year		Avg. Gal./ Boat		Gal./ Year	Brand	Est. % of Total
Boatyard							
1	550	x	1	=	550	Brolite Z-Spar	80
2	600		0.5		300	Pettit	20
2	600		0.5		300	Pettit	100
3	1,040		1		1,040	Brolite Z-Spar	44
						Woolsey	20
						International	36
4	500		1		500	Brolite Z-Spar	60
						International	20
						Woolsey	15
						Pettit	5
5	600		1		600	International	40
						Woolsey	55
						Brolite Z-Spar	5
6	110		1.25		140	International	65
						Brolite Z-Spar	35
7	180		2		360	International	98
						Brolite Z-Spar	1
						Pettit	1
8	500		1.5		750	Brolite Z-Spar	50
						International	50
9	790		1		790	Brolite Z-Spar	45
						Mariners	35
						Pettit	45
						Woolsey	10
						International	5
10	560		0.5		280	Brolite Z-Spar	45
						Woolsey	45
						Pettit	10
11	100		3		300	Brolite Z-Spar	100
12	100		0.75		75	Pettit	100
TOTAL	5,630				5,680		
Paint Retailer							
1	–		–		300	Mariners	50
						Woolsey	50
2	–		1		3	Kuhls	100
3	–		0.75		600	Pettit	100
4	–		–		10	Brolite Z-Spar	–
						International	–
5	–		2		700	International	60
						Brolite Z-Spar	40

Table 5b (Continued)

Supplier	Boats per Year	Avg. Gal./ Boat	Gal./ Year	Brand	Est. % of Total
Paint Retailer (Cont.)					
6	–	–	1	Pettit	100
7	–	1	–*	International	–
				Brolite Z-Spar	–
8	–	–	900	Brolite Z-Spar	75
				International	25
9	–	1	300	Pettit	45
				Mariners	35
				Woolsey	10
				Brolite Z-Spar	5
				International	5
10	–	–	1	Brolite Z-Spar	100

*No estimate available.

Table 6.

Estimated Use of Antifouling Paints for Ventura and Oxnard Marinas, 1973.

Supplier	Boats per Year	Avg. Gal./ Boat	Gal./ Year	Brand	Est. % of Total
VENTURA HARBOR					
Boatyard	330	1	330	–	–
Paint Retailer	–	–	50	Brolite Z-Spar	100
OXNARD/CHANNEL ISLANDS HARBOR					
Boatyard	480*	3.25	1,560	–	–

*Boatyard recently changed ownership; therefore, this estimate is believed to significantly underestimate past and future usage.

Table 7.

Estimated Annual Use of Antifouling Paints on Commercial and Naval Vessels in Los Angeles-Long Beach Harbor.

	Ships/Year			Gallons/Year				
Shipyard*	Commer-cial	Naval	Avg. Gal./Ship	Commer-cial	Naval	Total	Brand	Est. % of Total
1	38	2	–	2,605**	355**	2,960	International	40
							Devoe-Reynolds	60
2	0	24	–	0	4,650**	4,650	International	–
							Devoe-Reynolds	–
							Proline	–
3	300	0	20	6,000	0	6,000	International 1609	40
							Devoe-Reynolds	30
							Proline 1080	30
4	52	0	44	2,290	0	2,290	International	10
							Devoe-Reynolds	90
5	–	–	–	–	–	3,980†	–	–
6	–	–	–	–	–	3,980†	–	–
7	0	25	270	0	6,750	6,750	Devoe-Reynolds 121/63	90
							Devoe-Reynolds 129/63	10
TOTAL						30,600		

*All are commercial shipyards, except for Shipyard 7 (U.S. Navy).
**Obtained directly from company records.
†Assuming average value for Shipyards 1-4.

Table 8.

Estimated Annual Use of Antifouling Paints on on Commercial and Naval Vessels at Two of the Largest Shipyards in San Diego Harbor, 1972

	Commercial			Naval		
	Yard 1	Yard 2	Total	Yard 1	Yard 2	Total
Ships per Year	24	3		2	4	
Average Gallons per Ship	40	3,000		300	500	
Gallons per Year	960	9,000	9,960	600	2,000	2,600

Soxhlet Extraction Method. This method was used only when the separatory funnel method could not be used. The wet paint sample was spread out on aluminum foil and allowed to dry. After drying, the sample was extracted using the same method as that used on dry paint samples.

Dry Paint Extraction Method. Dry paint samples were Soxhlet extracted with hexane. The thimbles and hexane were added to the Soxhlet extraction apparatus, and the hexane was refluxed for a period of 2 hours to clean the apparatus. The rinse hexane was removed and replaced with clean hexane, and the samples were weighed into the cleaned thimbles. The Soxhlets were then refluxed for an 18-hour period. The extracts were concentrated in a Roto-vapor to a volume suitable for the Florisil clean-up column.

Florisil Cleanup. Activation of the Florisil was carried out using a pottery kiln. The temperature was set at a dial reading of 1300°F (705°C); this temperature setting on the kiln melts aluminum foil (which has a melting point of 659°C) and appears to be a satisfactory setting for the activation of Florisil. The Florisil was placed in 250-ml covered cricibles in the kiln and was baked for 4 hours after the kiln reached equilibrium tempera-ture. The activated Florisil was stored under hexane until use.

Three inches of the slurried-activated Florisil were added to the cleanup chromatographic columns,* and 1/2 inch of anhydrous sodium sulfate was added over the Florisil. Samples were concentrated to a volume of approximately 50 ml and added to the Florisil column. The column was eluted with 45 ml of 6 percent diethyl ether in hexane.

Extraction Efficiency. One paint chip sample (Code P17, Table 10) with a high PCB concentration (about 15 percent on a dry weight basis) was extracted and re-extracted with a Soxhlet extraction apparatus. The PCB value for the second extraction was 0.01 per-cent of the total value of the first extraction. If all dried

* 25 mm o.d., 22 mm i.d., 400 mm length with sealed-in coarse porosity fritted disc, Kontes Glass Co., Vineland, N.J.

paint samples are assumed to have the same permeability, then the procedure for dry paint extraction may be assumed to be highly satisfactory. Because none of the wet paint samples analyzed showed any appreciable concentration of PCB, it was not possible to quantify extraction efficiency for such samples. However, double extractions were conducted on a number of wet paint samples. Based on the relative signals obtained in the double extractions, and the very high recovery observed for the dry paint sample, we concluded that the PCB concentrations (usually upper limit values) listed in Table 9 are representative.

RESULTS

Sample descriptions, measured PCB concentrations, measured densities, weight percentages of copper compounds listed on paint can labels, and estimated metallic copper content are presented in Table 9. Table 10 lists PCB concentrations measured in weathered antifouling paint samples obtained at boat haul-out yards.

Because no DDT compounds were ever identified in the paint samples, upper limit concentrations were not calculated. Such values could be estimated to be approximately one-tenth of the maximum PCB 1254 values.

DISCUSSION

Antifouling Paint Usage

As seen from the data presented in Table 1, the 1971 inventory of small craft harbored at marinas throughout the Bight generally was confirmed by the 1973 inventories conducted at Oxnard Harbor, Marina del Rey, and Newport Bay. The percentage increases in numbers were 5, 9, and 7 percent, respectively. Assuming that the median value of 7 percent for percentage increase over the 2-year period is representative, approximately 37,000 recreational boats* were harbored in southern California marinas during 1973. The intensive surveys conducted at Marina del Rey and Newport Bay, which together account for about 40 percent of this total, yielded remarkably similar results. For example, the 4,100 small craft painted in the two boatyards at Marina del Rey during 1973 constituted 68 percent of the total number of boats (6,000) harbored there. In comparison, the 5,630 small craft painted at the 12 boatyards at Newport Bay constituted 66 percent of the total number (8,600) harbored at the Bay during 1973. Similarly, the median values for estimated gallons of antifouling paint applied per boat at both anchorages and for both haulout yards and paint retailers were 1 gal./boat.

As discussed in the previous section, at Marina del Rey, the boatyards apparently accounted for about 90 percent of the antifouling paint used at the marina, and retail sales to individuals for pri-

* Generally between 16 and 65 ft (5 to 22 m) in length.

Table 9.

Measured Polychlorinated Biphenyl Concentrations and Estimated Copper Concentrations in Antifouling Paints Used in Southern California.

Code	Brand and Type	Extraction Method*	PCB (mg/l) 1242	PCB (mg/l) 1254	Cu_2O (%)	ρ (kg/l)	Cu (g/l)
Recreational							
	Brolite Z-Spar						
P23	2000	A	<0.06	<0.16	32.6	1.73	500
P48	Multitox	A	<0.05	1.6	35.7	1.70**	540
P34	Colortox	B	-	0.29	0	-	0
P50	Supertox	-			59.4	1.70**	900
P53	Killer (B-90)	A	<0.3	<0.6	69.0	1.70**	1,040
P40	Racing Bronze	-			26.7†	1.13	300
P27	Vinyl Cop	-			-	-	-
P37	A-1316 (1969)	-	<0.4	<1.2	-	-	-
	Woolsey						
P24	Vinelast (Blue)	A	<0.3	<1.0	42.0	1.63	610
P39	Vinelast (Red)	A	<0.1	<0.3	42.0	2.08	780
P1	OTT	-			0	-	0
P44	Tradewinds	-			24.0††	1.50	390
P46	Racing Finish	-			42.0	1.47	550
-	Super-Vinelast	-			48.0§	1.70**	730
P33	Neptune	-			68.0	2.68	1,620
-	Foul-Ban	-			40.0	1.70**	600
	International						
P28	Inter-lux 62	B	<0.2	<0.6	31.5	1.70**	480
P26	Bottomkote 69	A	<0.4	<1.1	43.5	1.92	740
P20	Vinyl-lux	A	<0.03	<0.07	45.0	2.24	900
P19	Tri-lux	B	<0.3	<1.0	0	1.70**	0
P18	Copper-lux	A	<0.06	<0.15	67.5	2.83	1,700
-	Inter-club	-			31.5	1.70**	480

*A = separatory funnel method; B = Soxhlet method.
**Median density assumed.
†Percent metallic copper.
††Plus 9% CuOH.
§Plus 3% CuOH.

Table 9 (Continued)

Code	Brand and Type	Extraction Method*	PCB (mg/l) 1242	PCB (mg/l) 1254	Cu_2O (%)	ρ (kg/l)	Cu (g/l)
	Pettit						
P25	Unepoxy	B	<0.01	<0.03	60.7	2.30	1,240
P51	Trinidad 75 (Red)	A	<0.09	<0.2	75.8	1.79	1,210
P31	Pacific Special	A	1.7	1.2	35.0	1.66	520
P41	Old Salem	-			55.2	1.10	540
P36	Vinylcide red Starline Antifouling Bronze	-			0	-	0
	Mariner's						
P2	1034 Lido	A	<0.3	<0.6	68.1	1.76	1,060
	Singapore						
P32	696 Blue	A	<0.4	<1.2	34.0	1.54	470
	Devoe-Reynolds						
P30	Navicote	A	<84	<220	47.8	2.20	940
P63	Triple C	A	12.0	28.0	24.6	1.51	330
Commercial							
	Devoe-Reynolds						
P54	Super Tropical	A	18	23	24.6	1.88	410
P58	3407	A	<0.005	<0.023	38.5	2.58	880
P59	213	A	<0.92	<0.29	36.2	1.70**	550
P60	121	A			70.3	1.74	1,100
P64	Hot Plastic	B	1.30	3.00	32.5	1.20	350
P55	Cold Plastic 105	B	<1.6	<4.0	40.3	1.34	480
-	3402	-			10.0	1.70**	150
	Amarcoat						
P62	Emeron 67	A	1.20	2.80	15.0	1.51	200
	Proline						
P57	1080	A	<0.17	<0.72	51.0	1.70**	770
Navy							
	Devoe-Reynolds						
P60	121/63	A	<0.1	<0.4	70.3	1.74	1,090
P61	129/63	A	<0.1	<0.4	63.2	1.24	690

*A = separatory funnel method; B = Soxhlet method. **Median density assumed.

Table 10.

Concentrations of Polychlorinated Biphenyls Measured in Bottom Paints Removed from Boats in Southern California Drydocks.

Boatyard	Code	Origin	Method	PCB (mg/dry kg) 1242	PCB (mg/dry kg) 1254
Marina del Rey					
No. 1	P9	Fiberglass Hull	Sandblast	<0.1	3.0
	P10	Trashcan	Scrape	1.3	1.4
	P11	Trashcan	Scrape	9.5	3.5
	P12	Drain 1	-	<28	3,300
	P13	Drain 2	-	7.5	8.3
	P14	Drain 2	-	110	160
	P15	Wood Hull	Scrape	-	19
	P16	Wood Hull	Scrape	3,000	5530000
	P17	Wood Hull	Scrape	-	150,000
	P21	Yard	Scrape	<2.8	<0.3
	P22	Wood Hull	Scrape	<0.9	20
No. 2	P4	Wood Hull	Sandblast	<1.1	<1.1
	P8	Fiberglass Hull	Sandblast	<1.0	<4.2
Long Beach Harbor					
No. 5	P65	Wood Hull	Scrape	0.5	0.8
	P66	Wood Hull	Scrape	3.7	1.9

vate use accounted for the other 10 percent. Applying this factor to the boatyard statistics presented above, it is estimated that approximately 75 percent of the boats inventoried in the marinas of the Bight are painted annually, using on the average about 1 gal. of antifouling paint per boat. This implies that the application rate of antifouling paints to recreation craft along the southern California coast during 1973 was approximately:

$$37{,}000 \text{ boats inventoried} \times 0.75 \frac{\text{boats painted per year}}{\text{boats inventoried}} \times 1 \frac{\text{gallon paint}}{\text{boats painted}}$$

$$= 28{,}000 \text{ gal./yr}^*$$

Regarding the annual use of antifouling paint for commercial and naval vessels, as seen in Table 7, the estimated total for Los Angeles-Long Beach Harbor (San Pedro Bay) is 30,600 gal./yr. Table 8 presents data obtained for 1972 from records of the two largest shipyards in San Diego Bay; approximately 12,600 gal. of antifouling paint were used at these yards during that year. These results are in excellent agreement with those reported by Barry (1972) for the previous year; during 1971, a total of approximately 13,000 gal. of antifouling paint were applied to commercial and naval vessels in these two yards. As Barry's data imply that the total value for such vessels (excluding recreational craft) painted during 1971 in the Bay was approximately 19,400 gal., the estimated total annual use of antifouling paint on commercial and naval vessels at shipyards in the two bays is:

San Pedro Bay	=	30,600 gal./yr
San Diego Bay	=	19,400 gal./yr
Total	=	50,000 gal./yr

These two harbors contain the major shipyards located along the southern California coast.

PCB and Copper Inputs

As seen from Table 9, PCB 1242 or 1254 were detected in only 7 of the 28 wet paint samples analyzed. With the exception of Samples P54 and P63, whose total PCB concentrations each were approximately 40 mg/l, levels generally were the order of 1 mg/l or below. (Neglecting inequality signatures in Table 9, median values for PCB 1242 and 1254, were 0.3 mg/l and 0.7 mg/l, respectively.) When we combine these median values with the estimated quantities of antifouling paint applied annually to recreational, commercial, and naval vessels in marinas or harbors of the Bight, we obtain the estimated upper limits for PCB annual usage at each of the southern California anchorages shown in Table 11.

* One gallon equals 3.78 liters.

A corresponding calculation may be made for estimated copper usage. From the data presented in Table 9, the following summary of copper concentrations in antifouling paints is obtained:

Class	No. of Values	Cu (g/l)
Recreational	29	Median = 550 Range = 0-1,700 Mean = 660 $S_{\bar{x}}$ = 82
Commercial	9	Median = 480 Range = 150-1,100 Mean = 540 $S_{\bar{x}}$ = 110
Navy	2	Median = 890 Range = 690-1,090 Mean = 890 $S_{\bar{x}}$ = 200
Combined	40	Median = 550 Range = 0-1,700 Mean = 650 $S_{\bar{x}}$ = 655

These results are in reasonable agreement with those of Barry (1972); from his data, median concentrations for the above four categories are 610 (n = 21), 670 (n = 6), 1240 (n = 2), and 640 (n = 29). Although the naval vessel paints apparently contain somewhat more copper than do most paints used on the other types of craft, the results are generally quite similar. Until better data on usage of individual paints become available, it appears adequate to apply an average value for the copper content of antifouling paints used in the Bight. Combination of the results from Barry's study (overall median = 550 g/l) and from our study (overall median = 640 g/l) results in an estimated typical copper level of about 600 g/l. Using this figure, the estimated annual application rates of copper to vessel bottoms in each anchorage of the Bight have been calculated and are also listed in Table 11.

In Table 12, potential input rates of PCB and copper to the Bight through vessel paints are compared to those estimated for municipal wastewater (1971 data) and surface runoff (Water Year 1971-72) entering our coastal waters (Southern California Coastal Water Research Project 1973).

Table 11.

Estimated Annual Application Rates of PCB 1242, PCB 1254, and Copper to Recreational, Commercial, and Naval Vessels via Antifouling Paints at the Major Marinas and Harbors of the Bight, 1973.

Area	Anchorage	Paints* (gal./yr)	PCB (g/yr)** 1242	1254	Total	Copper† (metric tons/yr)
I	Santa Barbara Harbor	6600	0.7	1.6	2.3	1.4
II	Ventura Harbor	750	0.8	2.0	2.8	1.7
	Oxnard Harbor	750	0.8	2.0	2.8	1.7
III	Marina del Rey	4,410	5.0	12	17	10
	Redondo-King Harbor	1,120	1.3	3.0	4.3	2.5
V	Huntington	2,560	2.9	6.8	9.7	5.8
	San Pedro Bay	37,200	42	98	140	84
	Newport Bay	6,410	7.3	17	24.3	15
VI	Dana Point Harbor	440	0.5	1.2	1.7	1.0
	Oceanside Harbor	440	0.5	1.2	1.7	1.0
VII	Mission Bay	1,200	1.4	3.2	4.6	2.7
	San Diego Bay	22,100	25	58	83	50
	TOTAL	77,980			<294	177

*Assuming (1) a 7% increase in the 1971 inventory values for recreational craft listed in Table 1; (2) 75% of the recreational craft are painted annually, using an average of 1 gal. of antifouling paint per boat. The values for San Pedro Bay and San Diego Bay (30,600 and 19,400 gal./yr, respectively) include estimates for commercial and naval vessels. One gallon is equivalent to 3.78 liters.

**Upper limit figures, based on median values not exceeding 0.3 and 0.7 mg/l for PCB 1242 and PCB 1254, respectively.

†Assuming that, on the average, the concentration of copper in antifouling paint is about 600 g/l.

Table 12. Estimated recent annual input rates of PCB and copper to seven coastal areas of the Bight via municipal wastewaters and surface runoff, and estimated application rates of vessel antifouling paints.

Area	Total PCB (kg/yr)			Copper (m tons/yr)		
	Waste-waters*	Runoff**	Paints	Waste-waters*	Runoff**	Paints
I	-	1	0.01	--	0.6	1.4
II	3	10	0.01	1	8	3.4
III	570	18	0.02	190	3	12.5
IV	6,000	-	-	290	-	-
V	3,000	214	0.17	66	6	105
VI	-	3	0.01	-	0.9	2.0
VII	110	-	0.09	20	-	52.7
TOTAL	9,700	250	0.3	570	19	180

* 1971 data.
** Data from Water Year 1971-72.

CONCLUSIONS

Because 1971-72 was an unusually dry year, the estimated inputs for surface runoff (Table 12) are thought to be lower by about a factor of two than those that would have occurred under normal rainfall conditions. Also, source control efforts by the municipal wastewater managers apparently have now reduced the 1971 total PCB annual inputs by about a factor of two or three. Nevertheless, it is apparent that surface runoff probably is not an important source of either PCB or copper relative to municipal wastewater inputs.

While use of antifouling paints obviously now contributes a trivial amount of PCB to the harbors of the Bight (Table 12), the potential input (application rate) of copper via antifouling paint is seen to be quite significant. Overall, this potential input is about one-third the total estimate for municipal wastewater, and in Area V (San Pedro Basin) and Area VII (San Diego), it exceeds the wastewater value. Although we cannot yet estimate with any reliability what fraction of the copper contained in antifouling paint actually is released to the marine environment, the fact that this toxicant is deliberately added to the paint (in a matrix designed to gradually release the toxicant) to prevent fouling by marine invertebrates suggests that an important fraction of the copper applied is indeed released to the marine environment before re-painting. In addition, during repainting, a significant fraction of bottom scrapings may be blown or washed into the harbor water.

There is some indication that copper concentrations in digestive glands of the intertidal mussel and in the liver tissue of Dover sole collected from the vicinities of the major harbors in the Bight are somewhat higher than estimated baseline concentrations (Figures 8-19 and 7-14, Southern California Coastal Water Research Project 1973). This hypothesis is now being further investigated.

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