

SHORT PAPER

Butyltins in California river and lake marina waters

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Butyltins were analyzed in waters from California river and lake marinas and were detected at the part per trillion (ppt) level in most locations. The tributyltin:dibutyltin (TBT/DBT) ratios in the fresh waters were similar to those in their saline counterparts indicating like rates of degradation in the two salinity regimes.

Keywords: Butyltins, environment, analysis, marinas, fresh water

INTRODUCTION

Tributyltin (TBT) has been systematically analyzed in many California oceanic marinas.¹ As a consequence of its well documented impact upon non-target organisms in salt waters, the State of California has very severely regulated its use. However, there are few published analyses of its aqueous concentrations in fresh water marinas. Inasmuch as vessels in fresh waters have trivial fouling problems, i.e. primarily algal growth as opposed to the problem of barnacles, worms, etc., there is little reason to apply expensive TBT-containing antifouling paints. Still, the possibility of usage of such coatings and of their impact upon non-target organisms provided a foundation to initiate this program to analyze fresh waters from lake and river marinas for their TBT concentrations.

EXPERIMENTAL

Sample sites

Freshwater marinas (Fig. 1; the locations are indicated by parenthesized numbers in the text and Table 1) were selected in this study on the basis that they had berths

for 200 or more vessels.² Two exceptions were made: the Mobile Estates Marina (26) in the Salton Sea which is a hypersaline body and Lake Hodges (27) which is a reservoir, off San Diego, California, used as a source of potable water and used also as a site for pleasure boating.

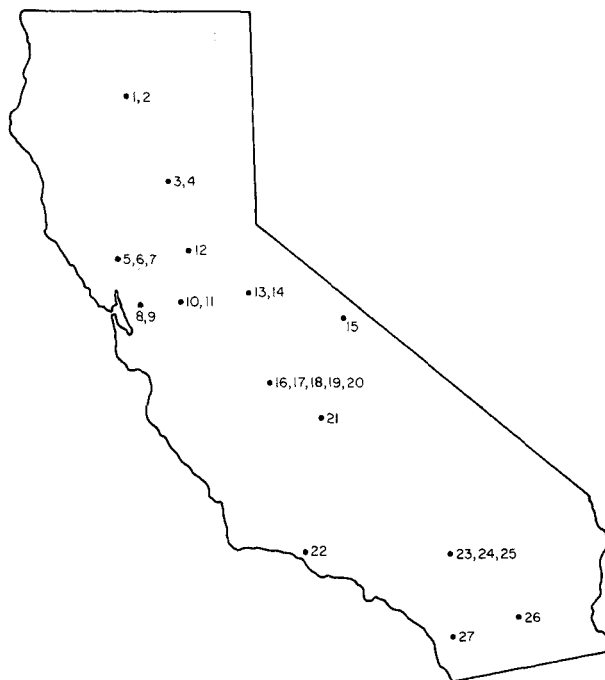


Figure 1 The locations of the sampling sites, by county. See Table 1 for details.

Samples of 500 cm³ volume were taken, usually at four sites in each marina. The samples were drawn from surface waters adjacent to the vessels. The bottles were filled by surface immersion and immediately placed in an ice-refrigerator. Upon return to the

Table 1 Butyltin analyses in California freshwater marinas (concentrations in nanograms/liter as cation)

Location and sampling date	No. of berths	TBT	DBT	MBT
Shasta County, Shasta Lake:				
(1) Bridge Bay Resort and Marina, 23 May 1988	734	9	8	nd
		4	2	nd
		8	2	nd
		7	2	nd
(2) O'Brien's Holiday Harbor, 23 May 1988	322	4	2	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
Butte County, Lake Oroville:				
(3) Bidwell Canyon Marina, 23 May 1988	200	3	nd	nd
		8	nd	nd
		19	nd	nd
		2	nd	nd
(4) Lime Saddle Marina, 23 May 1988	216	14	nd	nd
		9	nd	nd
		12	nd	nd
		19	nd	nd
Napa County, Lake Berryessa:				
(5) Steel Park Resort Marina, 24 May 1988	290	17	nd	nd
		22	nd	nd
		22	nd	nd
		14	2	nd
(6) Lake Berryessa Marina, 24 May 1988	210	nd	nd	nd
		6	2	nd
		2	nd	nd
		5	2	nd
(7) Rancho Monticello 24 May 1988	350	nd	nd	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
Contra Costa County, Holland Cut:				
(8) Holland Riverside Marina, 24 May 1988	355	nd	nd	nd
		7	3	nd
		26	10	5
		11	5	nd
Contra Costa County, India Slough:				
(9) Discovery Bay Yacht Harbor, 25 May 1988	266	62	30	5
		140	29	13
		34	14	nd
		29	13	nd
San Joaquin County, Buckley Cove:				
(10) Stevens Anchorage, 25 May 1988	Unknown	59	9	nd
		64	8	nd
San Joaquin County, San Joaquin River:				
(11) San Joaquin Sailing Club, 25 May 1988	300	110	29	9
		110	18	7

Table 1 (continued)

Location and sampling date	No. of berths	TBT	DBT	MBT
El Dorado County, Folsom Lake:				
(12) Brown's Ravine, 26 May 1988	650	nd	nd	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
Tuolumne County, Lake Don Pedro:				
(13) Lake Don Pedro Marina, 26 May 1988	350	5	nd	nd
		19	4	nd
		20	8	nd
		29	5	nd
Tuolumne County, Pinecrest Lake:				
(14) Pinecrest Lake Marina, 26 May 1988	200	17	nd	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
Mono County, Crowley Lake:				
(15) Crowley Lake Marina, 27 May 1988	234	7	2	nd
		4	nd	nd
		2	3	nd
		11	2	nd
Fresno County, Millerton Lake:				
(16) Millerton Lake Marina, 27 May 1988	500	17	10	3
		15	3	nd
		16	nd	nd
		12	3	nd
Fresno County, Shaver Lake:				
(17) Sierra Marina, 27 May 1988	200	nd	nd	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
Fresno County, Pine Flat Lake:				
(18) Trimmer Marina, 28 May 1988	300	nd	nd	nd
		nd	nd	nd
		nd	nd	nd
		nd	nd	nd
(19) Lombardo's Lakeview Resort, 28 May 1988	258	4	2	nd
		3	2	nd
		6	2	nd
		2	nd	nd
(20) Lakeridge Marina, 29 May 1988	260	nd	nd	nd
		4	3	nd
		4	3	nd
		3	2	nd
Tulare County, Lake Kaweah:				
(21) Kaweah Marina, 29 May 1988	268	nd	nd	nd
		nd	nd	nd
		nd	nd	nd

Table 1 (continued)

Location and sampling date	No. of berths	TBT	DBT	MBT
Ventura County, Lake Casitas:				
(22) Lake Casitas Recreational Area, 29 May 1988	200	6 2 nd 4	2 nd nd 2	nd nd nd nd
San Bernadino County, Big Bear Lake:				
(23) Pleasure Point Landing, 30 May 1988	160	7 14	3 7	nd nd
(24) Holloways Marina, 30 May 1988	250	3 nd	3 nd	nd nd
(25) Pine Knot Landing, 30 May 1988	230	110 14 nd 12	9 8 nd 4	nd nd nd nd
Imperial County, Salton Sea:				
(26) Marina Mobile Estates, 30 May 1988	200	nd nd nd nd	nd nd nd nd	nd nd nd nd
San Diego County, Lake Hodges				
(27) Reservoir, 10 August 1988	Unknown	nd 3 nd nd nd	nd nd nd nd nd	nd nd nd nd nd

nd, Not detected.

laboratory they were kept in a refrigerator at about 0°C.

Methodology

The analyses of the three butyltins, tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) were carried out by the hydride generation/atomic absorption procedure of Hodge *et al.*,³ as modified by Stallard *et al.*⁴

The detection limits were: MBT, 2.4 ng dm⁻³; DBT, 1.6 ng dm⁻³; and TBT, 2.0 ng dm⁻³. A 250-cm³ portion of each sample was diluted with 250 cm³ of butyltin-free seawater prior to analysis. The standard deviations for five replicate analyses of standards in the 6–10 ng dm⁻³ range were: TBT, 15%; DBT, 7%; and MBT, 10%.

RESULTS

The results are presented in Table 1. Several points are of interest. First of all, there are measurable amounts of TBT, and its degradation products DBT and MBT, in the majority of waters from lake and river marinas. The highest values were found at the Discovery Bay Yacht Harbor and at the San Joaquin Sailing Club with levels up to 140 ng dm⁻³. Both of these marinas berth vessels that can travel downriver to marine areas and perhaps this explains the use of TBT containing antifouling paints.

On the other hand, marinas from which there is no adit to marine waters (Millerton Lake Marina, Lake Don Pedro Marina, Lime Saddle Marina, Steele Park Resort Marina, Pine Knot Landing and Bridge Bay Resort and Marina) also have measurable TBT con-

Table 2 Frequency of TBT/DBT ratios in fresh and marine waters in percentage terms (marine data from Ref. 1)

Interval	Fresh water	Marine
Under 1	2	5
1 to 2	19	28
2 to 3	35	29
3 to 4	12	14
4 to 5	9	9
5 to 6	9	3
6 to 7	5	4
7 to 8	5	2
8 to 9	2	1
9 to 10	0	1
Greater than 10	2	4
	100	100

centrations in their waters, most probably from the bottom paints on the berthed vessels. There is really no reason to use these expensive TBT-containing paints on boats that never experience marine waters.

Finally, it appears that the average rate of TBT degradation in fresh waters is about the same as it is in marine waters on the basis of the TBT/DBT ratios

(Table 2). Thus, the parameters that govern degradation, viz. flushing times of the marine waters, water temperatures, photodegradation, bacterial degradation and sedimentation, do appear to combine to produce similar TBT/DBT ratios in both California domains.

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