include at least three to five events in the Cambrian [A. R. Palmer, *J. Paleontol.* **39**, 149 (1965); M. E. Taylor, *ibid.* **42**, 1319 (1968); J. H. Stitt, *ibid.* **45**, 178 (1971)], an Early Jurassic (Toarcian) event [A. Hallam, *Paleobiology* **3**, 58 (1977)], a terminal Eocene event [H. Tappan and A. R. Loeblich, *Geol. Soc. Am. Spec. Pap.* **127**, 247 (1971); A. G. Fischer and M. A. Arthur, *Soc. Econ. Paleontol. Mineral* **25**, 19 (1977)], and possible events in the latest Jurassic (Tithonian) and early Late Cretaceous (Cenomanian) (see A. G. Fisher and M. A. Arthur, above).

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28 September 1981; revised 31 November 1981

Lumber Spill in Central California Waters: Implications for Oil Spills and Sea Otters

Abstract. *A large quantity of lumber was spilled in the ocean off central California during the winter of 1978, and it spread through most of the range of the threatened California sea otter population within 4 weeks. The movement rates of lumber were similar to those of oil slicks observed elsewhere. These observations indicate that a major oil spill could expose significant numbers of California sea otters to oil contamination.*

The California population of the sea otter [*Enhydra lutris nereis* (Merriam)] was listed as "threatened" in 1977 (*1*) pursuant to the Endangered Species Act of 1973 (*2*). The listing was based on the possibility that a major oil spill could occur within the sea otter range and could kill a significant portion of the population, placing it in danger of extinction. This concern arises from the known sensitivity of the species to oil contamination (*3*). A spill of gasoline and diesel oil nearshore in the Kurile Islands, U.S.S.R., spread through 40 km of coastline and killed over 100 sea otters (*4*). Concern for the status of the California sea otter is heightened by the lack of evidence of significant population growth since 1973 (*5*).

It is difficult to project the critical day-to-day movements of floating oil near the sea otter range on the basis of existing oceanographic data. Surface current patterns off central California (San Francisco to Point Conception) have been examined with several techniques (*6–9*). The principal result is the description of mean flow patterns on a seasonal scale. However, studies of drogues and remote imagery have shown that short-term departures from mean seasonal drift may be frequent in the California current system (*6, 7, 10, 11*). Such departures involve tidal oscillations and mesoscale meanders and eddies (*6, 7, 10, 11*). The prediction of the direction of drift of floating oil is further complicated by the dominant role of wind stress at the air-sea interface (*12*). As far as we know, there are no records of major oil spills off central California on which to base predictions of oil drift. We know of no published studies of day-to-day movements of other floating materials off central California over an appropriately small time scale.

In this report we describe the movements and beaching of a large volume of lumber spilled off central California in the winter of 1978. Floating materials such as drift cards and plastic sheets have been used successfully by others in modeling the movements of oil on the sea surface (*13*). Our data provide a first approximation of the disposition of the floating component of a large oil spill occurring under similar conditions of weather and sea. Information of this kind is needed if we are to understand the potential impacts of oil spills on the California sea otter population and to develop management plans for improving the status of the population, now numbering about 1800 animals (*5*).

A cargo of 2×10^6 board feet of finished lumber (volume equivalent to 2.9×10^4 barrels of oil) spilled from a barge under tow in heavy weather 40 km west of Point Sur on 12 February 1978 (*14*). The spilled lumber was hazardous to navigation (*15*) and was therefore monitored by aircraft and merchant vessels in subsequent weeks (*16*). We compiled a record of observations of the floating lumber at sea along with sightings of lumber washed ashore after the spill.

Much of the spilled lumber remained in a single large patch that moved first toward the coast and then southeastward, parallel to the shoreline, during the first 10 days after the spill (Fig. 1). By 24 February the major patch was within 7 km of shore near Point Estero and remained relatively close to shore for the balance of the observation period (through March). Other patches of floating lumber were seen off Monterey, Point Lobos, Cape San Martin, and Point Arguello during the survey period. Beached lumber was found throughout two sections of coastline within the sea otter range, a northern section of about

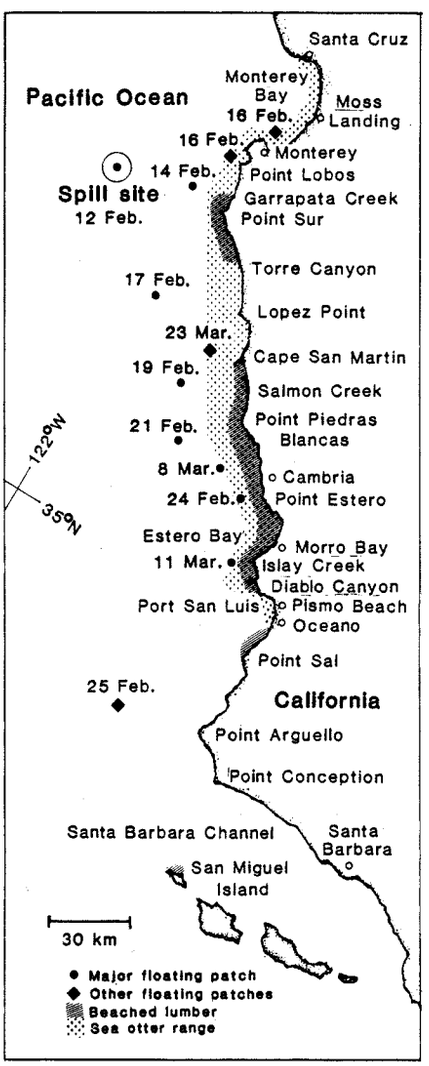

Fig. 1. Sightings of the major patch and smaller patches of floating lumber and areas of significant lumber beaching in and near the range of the sea otter population in California. Observations were made after the spillage of 2×10^6 board feet of lumber off Point Sur on 12 February 1978. All sightings of beached lumber were recorded between 12 February and 31 March 1978. The times and the positions corresponding to each sighting of the major patch of floating lumber are as follows: 12 February, 0650 GMT 36°15′N, 122°25′W (spill site); 14 February, 1930 GMT, 36°19′N, 122°07′W; 17 February, 0130 GMT, 35°55′N, 121°51′W; 19 February, 2030 GMT, 35°40′N, 121°37′W; 21 February, 0136 GMT, 35°29′N, 121°29′W; 24 February, 2100 GMT, 35°27′N, 121°05′W; 8 March, 1816 GMT, 35°30′N, 121°16′W; 11 March, 2006 GMT, 35°18′N, 120°58′W. Mean wind speed (meters per second) and the direction (relative to true north) between sightings of the major floating patch, during the period when the patch was closest to shore, were as follows: 21 to 24 February, 3.57, 317°; 24 February to 8 March, 0.90, 154°; 8 to 11 March, 4.30, 308° [wind data are from the shore station at Point Piedras Blancas (*18, 19*)].

0036-8075/82/0319-1503$01.00/0

42 km (Garrapata Creek to Torre Canyon) and a southern section of about 120 km (Cape San Martin to Diablo Canyon). These two sections comprise about half the sea otter range in California and contain about 47 percent of the otter population (*17*). Additional beached lumber was found between Oceano and Point Sal, and a large quantity washed ashore on San Miguel Island, primarily from Simonton Cove westward to Point Bennett. The beaching of lumber began near Point Sur in the northern section within 7 days of the spill. Significant quantities did not appear in the southern section until 10 to 13 March, a period characterized by strong northwesterly winds (*18*). Beached lumber was first seen at San Miguel Island in early March. No observations of floating lumber were recorded after 23 March.

Observations of floating petroleum either lost in major spills or released in experimental studies indicate that oil on the sea surface typically moves downwind at speeds of 1 to 5 percent of the wind speed (*12*). Data for wind velocities at sea near the floating lumber patches were not collected. However, we have examined shoreline wind data collected at Point Piedras Blancas (35°40′N, 121°17′W) during the observation period (*19*). From 21 February to 11 March, the largest patch of floating lumber was closest to shore and moved approximately downwind at speeds of 2 to 3 percent of the vector mean wind speed for each period between sightings.

Oil on the sea surface is physically and biologically altered on a scale of days to tens of days (*20*). It is therefore not clear that a large oil slick could persist in a form dangerous to sea otters for sufficient time to contaminate the entire range in California. Light, rapidly weathered oils spilled at a single location over a short time period should provide only a local threat to sea otters. However, our data on the drift of floating lumber indicate that it is possible that sustained spillage of heavy, persistent oils [for example, many types of crude oil (*20*)] would contaminate much of the sea otter's range. The most damaging spills would be wellhead blowouts and prolonged spillage from grounded supertankers, especially in areas subject to strong or shifting winds (*21*).

Our data indicate that the onshore movement of floating materials can be rapid, although prevailing winds run parallel to the shore in central California (*6, 18*). Thus, oil spills far from shore could threaten the sea otter population, most of which is located within 1 km of shore (*22*). Data from drift card and bottle studies indicate, however, that floating materials spilled more than 75 km from shore are not likely to wash ashore (*9, 11*). Within 75 km of shore, onshore movement of floating materials during winter is aided by strong southerly or southwesterly winds often associated with Pacific frontal systems and by milder southwesterly winds that frequently prevail for 1 to 2 days after the passage of fronts (*18*). Propagation of meanders and eddies from the shoreward edge of the California Current may promote the onshore transport of floating materials during any season (*6, 7, 10, 11*).

Major terminals servicing oil tankers up to 5×10^4 deadweight tons (DWT) exist at Moss Landing, Estero Bay, and Port San Luis, all within the sea otter range. Tanker traffic between California ports operates without established traffic separation schemes, and roughly one-quarter of the tanker masters run their vessels within 8 km of shore off Point Sur (*23*). Large tankers (to 7×10^4 DWT) bearing crude oil from the trans-Alaska pipeline use established traffic patterns along central California en route to ports farther south. Southbound tankers from Alaska pass a minimum of 65 km from shore off Point Piedras Blancas (*23*). Outer Continental Shelf Oil Lease Sale 53 began in 1981, and, pending the outcome of litigation, such sales could lead to the development of offshore oil production and transport facilities within the sea otter range by 1986 (*24*). Outer Continental Shelf Oil Lease Sales 68 and 73 are scheduled for 1982 and 1983, respectively, and could include tracts within the range of the sea otter (*25*). Two to three major oil spills are expected to result from oil production on the outer continental shelf (*26*).

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18 August 1981; revised 30 November 1981

Methylation of Tin by Estuarine Microorganisms

Abstract. *Mixed inoculums of microorganisms from Chesapeake Bay sediments transformed inorganic tin ($SnCl_4 \cdot 5H_2O$) to organotin compounds. Dimethyltin and trimethyltin species were identified as products by gas chromatography–mass spectrometry. Methylated tin species were not observed in sterile controls or in poisoned controls. Thus, estuarine microorganisms have the potential for transforming tin to toxic organotins and for mobilizing tin in the ecosystem.*

Tin was one of the first metals used by man; implements made of tin alloy date as far back as 3000 B.C. (*1*). Today, inorganic tin is used as a protective coating for steel and in solders, bearing metals, and other alloys. Organotin compounds are used as stabilizers for polyvinyl chloride plastics. They are also incorporated into biocidal preparations such as insecticides, herbicides, fungicides, and antifouling paints (*2*). Most of these compounds will eventually enter the environment where they can be leached from consumer products by chemical and biological (mainly microbiological) processes. Organotins are toxic to eukaryotes (*3*) and prokaryotes (*4*), but few studies have been done on the environmental distribution and transport of tin (*5–7*). A biological cycle for tin has been proposed (*8*) and discussed (*9*). The biotic and abiotic formation of $(CH_3)_4Sn$ from $(CH_3)_3SnOH$ in material taken from anaerobic sediments has been demonstrated recently (*10*), and methylstannanes have been found in Chesapeake Bay (*11*). The purpose of this investigation was to assess the potential of sediment microorganisms in Chesapeake Bay to biotransform inorganic tin to organotin compounds.

Sediment samples were taken in the summer of 1979 at nine sites in the northern and central Chesapeake Bay. The tin content of sediments at these sites varies with the amount of human activity at the site (*6*).

Two systems, flask cultures and Hungate tubes, were used to determine if the microbial flora could transform tin into volatile organometallic derivatives: 1) A 250-ml, screw-capped Erlenmeyer flask received 10 ml of solid nutrient medium (*12*) supplemented with 0.75 mg of tin as $SnCl_4 \cdot 5H_2O$. A sterile 10-ml beaker was placed in the center of the medium before it solidified. One milliliter of an 8 percent (weight to volume) solution of citric acid in 10 percent HCl was added to the beaker to trap volatile tin compounds. Each flask was then inoculated with 1.0 ml of a 1:10 (weight to volume) suspension of sediment in an estuarine salt solution (10.0 g of NaCl, 2.8 g of $MgSO_4$, and 0.3 g of KCl per liter of distilled water). The flask was closed and incubated for 14 days at 25° ± 2°C. Material in the beaker was then sampled and analyzed for tin by atomic absorption spectrophotometry (AAS).

2) Each Hungate tube (*13*), containing 5.0 ml of liquid nutrient medium (*12*) with 0.375 mg of tin as $SnCl_4 \cdot 5H_2O$ was inoculated with 0.5 ml of a 1:10 (weight to volume) suspension of sediment in estuarine salts and incubated for 14 days at 25° ± 2°C. The culture was then centrifuged to remove debris, and the supernatant medium was extracted with a dichloromethane-chloroform mixture (9:1, volume to volume). The organic phase was evaporated to dryness, and the residue was resuspended in methyl isobutyl ketone and analyzed by AAS.

Sterile controls containing $SnCl_4 \cdot 5H_2O$ gave negative results, and sterile controls in which $(CH_3)_2SnCl_2$ (75 mg of tin per liter) was substituted for $SnCl_4 \cdot 5H_2O$ yielded tin in the center well of flasks or the organic phase extracted from tube cultures. Thus, the two methods can be used to detect an organotin compound without interference by inorganic tin. For eight of nine sediment samples, the experimental flasks and tubes contained organotin compounds. For the ninth sample, taken from the Patuxent River, the culture did not produce evidence of volatile organotins. No organotin was detected in tubes or flasks containing the metabolic poison sodium azide. Therefore, the transformation of inorganic tin to organotin was the result of biological activity.

To identify the volatile tin compounds produced, we used larger volumes of culture. Flask cultures containing 500 ml of liquid medium (*12*) and 37.5 mg of tin as $SnCl_4 \cdot 5H_2O$ were inoculated with 0.1 g of sediment and incubated for 14 days. We analyzed the culture medium for organotin compounds by using a modified hydride reduction technique (*5, 7*). The medium was centrifuged, and 100 ml of supernatant medium was added to a gas scrubbing bottle. Using Tygon tubing, we attached a 0.2-m stainless steel chromatographic column (outside diameter, 6 mm; capacity, 2 ml) packed with Tenax GC (Supelco Inc., Supelco Park, Pennsylvania) to the bottle. The column was cooled to −40°C with liquid nitrogen. The spent medium was adjusted to *p*H 6.2 with 2*M* tris-HCl, and the solution was purged with N_2 for 2 minutes. Two milliliters of 1 percent (weight to volume) $NaBH_4$ was then added quickly, and N_2 was bubbled slowly through the solution. The bottle was immersed in a water bath at 90°C for 5 minutes. The column was then removed and allowed to warm slowly to approximately 0°C. A syringe was attached to the column with Tygon tubing, and the column was eluted with 10 ml of cold (4°C) heptane. The heptane solution was then stored at −10°C until it was analyzed. A gas chromatograph equipped with an electron-capture detector was used to separate and measure the organometallic species.

All three authentic methyltin hydrides [CH_3SnH_3, $(CH_3)_2SnH_2$, and $(CH_3)_3SnH$] and $(CH_3)_4Sn$ were resolved (Fig. 1). The extract from cultures inoculated with sediment contained two peaks which cochromatographed with $(CH_3)_2SnH_2$ and $(CH_3)_3SnH$ standards, respectively. A minor peak was also obtained that had a retention similar to that of CH_3SnH_3, but it was not detected in all replicate experiments. Sterile controls and cultures that received sodium azide yielded no metal hydride peaks. Thus, the organotins produced were the result of biological activity.

0036-8075/82/0319-1505$01.00/0