ZINC-65 AND DDT RESIDUES IN ALBACORE TUNA OFF OREGON IN 1969

WILLIAM G. PEARCY Department of Oceanography Oregon State University Corvallis, Oregon

and

ROBERT R. CLAEYS Department of Agricultural Chemistry Oregon State University Corvallis, Oregon

THE HYPOTHESIS

Albacore (*Thunnus alalunga*) is typically an oceanic tuna found far from continents. However, each summer a portion of the North Pacific population migrates into nearshore waters along the west coast of North America. Pearcy and Osterberg (1968) found that the zinc-65 radioactivity increased dramatically in albacore caught off Oregon and Washington during the summers of 1962–1966. This increase was attributed to the association of albacore with Columbia River water, a known source of radionuclides into these marine waters.

Manigold and Schulze (1969) reported DDT, DDE and DDD in Columbia River water during various seasons, 1966–1968. Sometimes levels of residues were 0.1 ppb (0.1 μ g/l), which is similar to those reported in the Sacramento River which drains agricultural lands where pesticides are heavily used.

Therefore, if the Columbia River is a major mechanism for transport of DDT and its metabolites to the ocean, then DDT as well as ⁶⁵Zn should increase with time while albacore inhabit nearshore waters off Oregon during the summer. Similar trophic pathways and uptake rates for DDT and ⁶⁵Zn are implicit in this hypothesis.

BACKGROUND

The Columbia River is the largest river on the Pacific coast of the Americas and the second largest in the United States. It discharges about 7,250 m³ per second of fresh water into the Pacific Ocean at the headwaters of the California Current (Leopold, 1962). The Columbia is also unique because until 1971 it carried distinctive radionuclides from the Hanford nuclear reactors into the ocean.¹ Columbia River water was used as a primary coolant for the reactors and the intense neutron flux of the reactors induced radioactivity of trace elements in the water. Stable zinc-64, for example, added a neutron and became radioactive zinc-65. Most of the radionuclides in the coolant water had short physical half-lives and decayed to undetectable levels during the 370 mile trip

to the ocean. Zinc-65 and chromium-51 (half lives of 245 and 28 days respectively) were the most common artifically induced radionuclides entering the Pacific Ocean (Osterberg, Pattullo and Pearcy, 1964; Gross, Barnes and Riel, 1965; Perkins, Nelson and Haushild, 1966; Osterberg, 1965).

The distribution of Columbia River water in the ocean varies with season and is dependent upon the direction of prevailing winds. During the summer, northerly winds predominate and Columbia River waters usually flow to the south or southwest as a "plume." The maximum discharge of the Columbia River usually occurs in June, and the plume can often be detected by low salinities far to the south of the mouth of the river (Barnes and Gross, 1966; Owen, 1968). With the onset of winter, the wind stress reverses and prevails from the south, resulting in northerly transport of Columbia River waters along the Washington coast. During this season the plume is not as obvious because of large runoff of coastal rivers (Barnes and Gross, 1966). Figures 1 and 2 illustrate the location of plume waters during the summer by salinity and the winter by chromium-51. The plume has been identified by chromium-51 and zinc-65 (Gross, Barnes and Riel, 1965; Osterberg, Cutshall and Cronin, 1965; Barnes and Gross, 1966), specific alkalinity (Park, 1966) and surface temperature (Owen, 1968; Pearcy and Mueller, 1970; Pearcy, in press).

Seasonal, geographic and bathymetric variations in the Zn-65 content of marine organisms off Oregon is correlated with the distribution of Columbia River waters at sea (Carey, Pearcy and Osterberg, 1966). Pearcy and Osterberg (1967) found seasonal maxima during the summer in Zn-65 of oceanic zooplankton and micronekton collected by midwater trawling in the upper 150 m off Oregon. These seasonal variations (see Figure 3) are believed to result from seasonal shifts in the location of plume.

Zinc-65 was ubiquitous in marine organisms radioanalyzed off Oregon (Osterberg, Pearcy and Curl, 1964; Carey, Pearcy and Osterberg, 1966). Of particular interest is the enhancement of Zn-65 in albacore tuna. Zinc-65 levels in albacore livers increased dramatically during the summer months off Oregon and Washington, whereas levels in albacore collected off

¹When this paper was written (February 1971) all nuclear reactors at Hanford were shut down.



FIGURE 1. Pattern of Columbia River plume based on surface salinity, June 18–July 3, 1969.

southern and Baja California were much lower and displayed no seasonal increase (Figure 4). This marked increase in Zn-65 levels off Oregon and Washington is attributable to albacore feeding on animals which have accumulated Zn-65 introduced into the ocean by the Columbia River. Albacore concentrations are also known to be located in the vicinity of plume waters, probably because plume waters are heated more rapidly than surrounding waters during the early summer (Owen, 1968; Pearcy, in press; Panshin, unpublished).

Because of the marked increase in Zn-65 in albacore after they migrated into Oregon waters and because of the DDT residues detected in Columbia River water (Manigold and Schulze, 1969), we examined albacore in 1969 for both radionuclides and pesticides.

METHODS

Albacore (550-730 mm fork length) were collected off the Oregon coast during the summer of 1969 on jigs trolled from the R/V YAQUINA and CAYUSE or the fishboats SUNRISE and TYPHOON. Livers were either removed from the albacore at sea and frozen in plastic bags, or whole albacore were frozen



FIGURE 2. Pattern of Columbia River plume based on chromium-51 activity of surface water, February 1966 (from Frederick, 1967).

and samples of livers and flesh obtained in the laboratory ashore. These samples were used for radioanalysis and pesticide analysis.

Procedures for radioanalysis were similar to those described by Pearcy and Osterberg (1968). Whole livers and samples of flesh were weighed, dried, ashed and packed in 15 cc counting tubes for radioanalysis in a 12.7 cm³ sodium iodide (TI) crystal coupled to a 512 channel pulse-height analyzer. Counting time was 100 or 400 minutes.

The predominant gamma emitter was zinc-65. To permit calculation of specific activity of zinc-65, total concentration of zinc was determined by atomic absorption spectrometry (Perkin-Elmer model 303) on samples of ash digested in nitric and hydrochloric acids.

Liver samples for pesticide analysis were obtained from lateral lobes, the median lobe, or entire homogenized livers. Flesh samples were taken near the body cavity. The tissue sample was diced and a 7-20 gram subsample was blended in an Omni-mixer with 25 ml of acetone and 1 gram of anhydrous Na₂SO₄ per gram of sample. After filtering the mixture through a Buch-



FIGURE 3. Zinc-65 radioactivity per gram wet weight from opening-closing midwater trawl samples from three depth intervals, 93 km off central Oregon coast, 1963–1965. Solid lines connect the average of nighttime collections, the dashed lines of daytime collections. Vertical lines show the range of values (from Pearcy and Osterberg, 1967).



FIGURE 4. Zinc-65 per gram of albacore liver ash off the west coast of North America during the summer of 1962 (□), 1963 (+), 1964 (●), 1965 (▲ Oregon, △ Washington), and 1966 (○). The distances in kilometers indicate how far albacore captured in the three regions were from the mouth of the Columbia River (from Pearcy and Osterburg, 1968).

ner Funnel, the vacuum was reduced, the filter cake covered with acetone, and vacuum was reapplied. One part water per part acetone was added to the filtrate and pesticides were extracted with 50 ml of pentane in a separatory funnel. The pentane layer was collected and an additional one part water and 50 ml of pentane were added for a second extraction. The combined pentane fractions were evaporated to 5–10 ml and loaded on top of a Florisil adsorption column for further separation.

The Florisil column was prepared by adding 25 ml of hexane to a 16 mm i. d. glass column fitted with a Teflon stopcock. Ten grams of -200 mesh, 450° C oven dried Florisil were stirred into the column and washed down with hexane. Then $\frac{3}{4}$ inch of anhydrous Na₂SO₄ was added.

Pesticides were eluted from the column with: 1st cut, 60 ml of hexane; 2nd cut, 75 ml of 5% benzene hexane (this eluant contains p, p'-DDE, o, p'-DDT, p, p'-DDT); 3rd cut, 75 ml of 20% benzene-hexane (contains p, p'-TDE); 4th cut, 60 ml of 15% diethyl ether, 0.25% acetone, 85% hexane; 5th cut, 90 ml of the 15% diethyl ether, 0.25% acetone, 85% hexane mixture (contains dieldrin and endrin). After initial analysis showed that DDE could elute into the first cut on occasion, the hexane elution was omitted. The 4th and 5th cuts were not analyzed routinely because of poor lipid separation and absence of pesticides.

The column eluant was analyzed for pesticides by gas-liquid chromatography using electron capture and microcoulometric detectors with a sensitivity (0.1 mv peak height) of 0.01 and 1.0 nanograms of p, p'-DDE respectively. A 122 cm (4 ft) x 2 mm i. d. pyrex column (fluorosilicone polymer) was packed with a 2.4:1.0 mixed packing of 7% QF-1 and 7% DC-11 (methylsilicone polymer) on 100/120 mesh Chromosorb W high performance for analysis.

The conditions for the electron capture gas chromatograph were: 210° C inlet temperature, 180° C column temperature, 200° C detector temperature and column gas (nitrogen) flow rate of 40 ml/min. The retention time of p, p'-DDE was approximately 4 minutes. The sample solution was analyzed in duplicate by injecting 2-8 µl subsamples into the gas chromatograph with a 10 µl syringe, followed by injections of 2-8 µl subsamples of 0.01, 0.02 or 0.04 ng/µl standard solutions. The amount of standard was selected to give a peak within 20% of the sample pesticide peak. The second injection of sample solution was either $\frac{1}{2}$ or twice as large as the first injection. A third analysis was required if the peak heights were not within 8% on a comparable basis.

Because of the very low levels of pesticides present, special precautions were taken to avoid contamination. Technical acetone was refluxed with $KMnO_4$ (0.5 g/l) for 1 hour and distilled. N-pentane and n-hexane were refluxed over sodium wire overnight before distillation. The Florisil adsorbent required purification and was placed in a muffle furnace at 450°C for 15 hours. All glassware was isolated and cleaned with K₂CrO₄-



FIGURE 5. Zinc-65 radioactivity (^O) and specific activity, ⁶⁵Zn/Zn (•) of ashed samples of albacore livers, 1969.

 H_2SO_4 cleaning mixture and rinsed with water and acetone. The anhydrous Na_2SO_4 was washed with hexane before use and the water was purified by hexane extraction prior to use. The contamination of the glassware and reagents was determined prior to use by analyzing "solvent blanks", i.e. following the above procedure without addition of tissue.

Our procedure for the elution of the Florisil column was selected for analysis of low levels of chlorinated hydrocarbons. Other reported procedures resulted in interferences in the gas chromatographic analysis.

The presence of DDT was confirmed by microcoulometric detection of halide compounds and by base hydrolysis which converts o, p' and p,p'-DDT to their respective DDE analogs. Base hydrolysis destroys TDE. Arochlors and samples containing 0.001 ppm or more of any of the DDT analogs could be detected by this procedure.

The presence of other chlorinated compounds, particularly the polychlorinated biphenyls (PCB's) was also investigated by microcoulometry after base hydrolysis of DDT. The PCB compounds are stable under the conditions used. PCB compounds were not found in our albacore samples above our detection level of 0.03^2 ppm.

RESULTS

Gamma-ray spectra revealed Zn-65 as the prominent artificial radioisotope present in albacore livers. Cesium-137, manganese-54 and cobalt-60 were also present. Figure 5 shows that the Zn-65 radioactivity per gram and the specific activity of Zn-65 of albacore livers increased greatly during the summer of 1969, thus reaffirming trends observed in previous years by Pearcy and Osterberg (1968). Slopes of linear regression lines fitted by least squares to both the untransformed and logarithms of radioactivity values are highly significant (P <0.01, n = 28).

Our analyses of DDT residues in albacore liver and flesh tissue are summarized in Table 1. The levels of all metabolites were low. p, p'-DDE was the most prominent residue. It was found in concentrations up to a maximum of 0.16 ppm and was present above blank values in all 41 samples analyzed. Chromatographic peaks attributable to p, p'-DDT; o, p'-DDT and p, p'-TDE were usually present. Although levels of these residues were lower than p, p'-DDE, most values were significantly above blank values. Low values of o, p'-DDT and p, p'-DDT may be influenced by PCB's. No dieldrin was detected above blank levels of 0.003 ppm. The average values for all DDT residues combined were 0.05 for liver (range 0.003-0.22) and 0.07 for flesh (range 0.004-0.22).

To our dismay, we discovered that liver tissue was not uniform in regard to DDE storage. Both lateral and median lobes from each of four fish were analyzed and the lateral lobes on the average contained about seven times more DDE than the long median lobes. Because of this large difference, we had to consider separately each type of liver sample.

The values for DDE and DDT in whole albacore livers and median lobes are plotted in Figure 6 to show any trends that occurred with time during the summer of 1969. Concentrations of DDE and DDT were highly variable (note the log scale). No pronounced changes in the average pesticide level are evident during the summer. The slope of regression lines fitted by least squares to the untransformed pesticide values are not significant (P > 0.5) for either DDE or DDT in the median lobes (n = 19), whole livers (n = 7), or in flesh (n = 11, not shown in Fig. 6).

Thus Zn-65 was significantly enhanced while albacore resided in coastal waters off Oregon during the summer of 1969, but DDT residues did not undergo a similar increase. The lack of positive correlations between Zn-65 and DDT or DDE further indicated the independence of these pollutants. Correlation coefficients were not significant (P > 0.05) among Zn-65 and p, p'-DDE, Zn-65 and p, p'-DDT, and Zn-65 specific activity and DDT. The correlation between specific activity and DDE, however, was significant (P = 0.05). These correlations were based on twelve comparisons of livers from individual albacore.

TABLE 1

DDT residues, parts per million, on a wet weight basis in albacore collected off Oregon, 1969. (B = equivalent to blank value)

Phin Phin												
	p, p'-DDE			o, p'-DDT			p, p'-TDE			p, p'-DDT		
	n	x	Range	n	x	Range	n	x	Range	n	x	Range
Whole livers	7	0.025	0.01- 0.05	4	0.005	B-0.01	4	0.007	0.004-	6	0.012	0.001-
Median lobe	19	0.023	0.001 0.14	9	0.009	B-0.026	9	0.004	0.004- 0.016	14	0.011	B-0.04
Lateral lobes	4	0.09	0.022 0.16									
Flesh	11	0.035	0.003- 0.14	7	0.012	B-0.028				11	0.02	0.001- 0.04
Blank values (per 5 gm samples)	4	0.0002	0.0003- 0.0028	4	0.0006	0.0002- 0.001	4	<0.0004		4	0.0008	0.0003- 0.003
Percent recoveries	4	93.7	90–113	3	96.3	94-98	4	88.3	83-94	4	90.3	86-93

² Since this paper was written, some extracts of whole livers have been reanalyzed for PCB's by an improved method. Values ranged from 0.02 to 0.03 ppm using 1260 formulation as a standard. Since many of the samples were collected in plastic bags and possibly contaminated with PCB's, these values must be suspect.

DISCUSSION

Our results indicate small amounts of DDT residues in albacore tuna and no significant increase in levels during their sojourn in Oregon waters in 1969, even though Zn-65 levels increased drastically as a result of their association with the Columbia River plume. Seasonal variations in the DDT residues of other fishes have been reported (Kelso *et al.*, 1970; Smith and Cole, 1971), indicating that rapid uptake of DDT is possible. Our hypothesis that the Columbia River is a major source of DDT for the ocean off Oregon is therefore rejected. The average values for total DDT residues in albacore were very similar to those reported by Risebrough (1969) for skipjack tuna (*Euthunnus pelamis*) off Hawaii and the Galapagos Islands. Thus we have no evidence that freshwater drainage into coastal waters is a major source for DDT contamination in albacore. Our results provide additional support for aerial transport as an important mechanism for transfer of chlorinated hydrocarbons into the oceans.

The lack of correlation between freshwater drainage from agricultural lands and DDT in marine fishes has been reported by Risebrough *et al.* (1967) and Risebrough (1969). They found that northern anchovy in San Francisco Bay contained less DDT





FIGURE 6. DDT residues and samples of albacore livers, 1969. The dashed line at 0.002 ppm represents twice our blank values for p, p'-DDT; any values recorded less than this are located on this line.

residues that those off southern California. Cox (this volume) found little evidence for elevated DDT residues in waters around the Columbia River plume. Aerial fallout and global atmospheric transport of DDT is further evidenced by DDT residues in airborne dust transported by the Atlantic trade winds (Risebrough et al., 1968), by DDT residues in rainwater, even from the agriculturally remote Shetland Islands (Tarrant and Tatton, 1968), by the occurrence of pesticides in Antarctic birds and mammals (Tatton and Ruzick, 1967), in seals and porpoises in Scotland and Canada far from sites of application (Holden and Marsden, 1967), in the Bermuda petrel (Wurster and Wingate, 1968), other shearwaters and other pelagic birds (Risebrough et al., 1967), and in sperm whales (Wolman and Wilson, 1970).

The ocean distribution of some radionuclides that were produced by nuclear explosions and transported by world-wide atmospheric circulation also indicate less accumulation of fallout in coastal waters. Pearcy and Osterberg (1968) found that manganese-54 levels decreased with time in albacore caught during the summer off Oregon. This trend suggested higher uptake of this fallout radionuclide in oceanic than in nearshore waters, a conclusion that was supported by the higher amounts of Mn-54 found in oceanic than coastal zooplankton. Pillai, Smith and Folsom (1964) and Folsom and Young (1965) found higher concentrations of other fallout radionuclides offshore than inshore. Thus fallout of some pollutants, including DDT, into oceanic regions far from the area of initial dispersal may actually be higher than into coastal seas.

Some conclusions of the recent Report of the Study of Critical Environmental Problems (SCEP, 1971, pp. 133, 135) provide an ideal ending for this paper but hopefully not an epitaph for the oceans. They concluded that "... DDT and its residues are most probably distributed throughout the marine biosphere ..." and "the atmosphere appears to be the major route for transfer of DDT residues into the oceans, ... and ultimate accumulation site of DDT and its residues".

ACKNOWLEDGMENTS

This research was supported in part by the Atomic Energy Commission (Contract AT (45-1) 2227, Task Agreement No. 12, RLO-2227-T12-1) and the National Science Foundation Institutional Sea Grant (GH45). We are grateful to Miss Erika Saunders who assisted in the chromatographic analyses, to William Renfro who made helpful editorial comments, and to the captains and crews of the TYPHOON, SUNRISE, CAYUSE AND YAQUINA who provided albacore for analyses.

REFERENCES

- Barnes, C. A. and M. G. Gross. 1966. Distribution at sea of Columbia River water and its load of radionuclides. In Disposal of radioactive wastes into seas, oceans and surface waters. Int. Atomic Energy Agency, Vienna 1966, p. 291-302.
- Carey, A. G., Jr., W. G. Pearcy and C. L. Osterberg. 1966. Artificial radionuclides in marine organisms in the Northeast Pacific Ocean off Oregon. In Disposal of radioactive wastes into seas, oceans and surface waters. Int. Atomic Energy Agency, Vienna, 1966, p. 303-319.
- Folsom, T. R. and D. R. Young. 1965. Silver-110 and cobalt-60 in oceanic and coastal organisms. *Nature 206:* 803-806.
- Frederick, L. C. 1967. Dispersion of the Columbia River plume based on radioactivity measurements. Ph.D. thesis, Oregon State Univ. Library, 109 pp.
- Gross, M. G., C. A. Barnes and G. K. Riel. 1965. Radioactivity of the Columbia River effluent. Science 149:1088-1090.
- Holden, A. V. and K. Marsden. 1967. Organochlorine pesticides in seals and porpoises. Nature 216: 1274-1276.
- Kelso, J. R. M., H. R. MacCrimmon and D. J. Ecobichon. 1970. Seasonal insecticide residue charges in tissues of fish from Grand River, Ontario. Trans. Amer. Fish. Soc. 99: 423-426.
- Leopold, L. B. 1962. Rivers. Amer. Sci. 50: 511-537.
- Manigold, D. B. and J. A. Schulze. 1969. Pesticides in selected western streams—a progress report. *Pesticide Moni*toring J. 3: 124–135.
- Osterberg, C., W. G. Pearcy and H. C. Curl, Jr. 1964. Radioactivity and its relationship to oceanic food chains. J. Mar. Res. 22: 2-12.
- Osterberg, C., J. Pattullo and W. Pearcy. 1964. Zinc-65 in euphausiids as related to Columbia River water off the Oregon coast. Limnol. Oceanogr. 9: 249-257.
- Osterberg, C. L. 1965. Radioactivity from the Columbia River. Ocean Science and Ocean Engineering (ASLO-MTS) 2:968-979.
- Osterberg, C. L., N. Cutshall and J. Cronin. 1965. Chromium-51 as a radioactive tracer of Columbia River plume water at sea. Science 150: 1585-1587.
- Owen, R. W., Jr. 1968. Oceanographic conditions in the northeast Pacific Ocean and their relation to the albacore fishery. U.S. Fish Wildl. Serv. Fish Bull. 66: 503-526.
- Panshin, D.A. 1971 Albacore tuna catches in the northeast Pacific during summer 1969 as related to selected ocean conditions. Ph.D. thesis, Oregon State Univ. Library, 110 pp.

Park, K. 1966. Columbia River plume identification by specific alkalinity. Limnol. Oceanogr. 11: 118-120.

- Pearcy, W. G. and C. L. Osterberg. 1967. Depth, diel, seasonal and geographic variations in zinc-65 of midwater animals of Oregon. Int. J. Oceanol. Limnol. 1: 103-116.
- Pearcy, W. G. and C. L. Osterberg. 1968. Zinc-65 and manganese-54 in albacore *Thunnus alalunga* from the west coast coast of North America. *Limnol. Oceanogr.* 13: 490-498.
- Pearcy, W. G. and J. L. Mueller. 1970. Upwelling, Columbia River plume and albacore tuna. Proc. Sixth Int. Symp. on Remote Sensing of Environment, pp. 1101-1113.
- Pearcy, W. G. 1971. Remote sensing and the pelagic fisheries environment off Oregon. Symp. on Remote Sensing in Marine Biology and Fishery Resources, College Station, Texas, pp. 158-171.
- Pearcy, W. G. in press. Albacore oceanography off Oregon, 1970. Fish Bull. U.S.
- Perkins, R. W., J. L. Nelson and W. L. Haushild. 1966. Behavior and transport of radionuclides in the Columbia River between Hanford and Vancouver, Washington. Limnol. Oceanogr. 11: 235-248.
- Pillai, K. C., R. C. Smith and T. R. Folsom. 1964. Plutonium in the marine environment. Nature 203: 568-571.
- Risebrough, R. W., D. B. Menzel, D. J. Martin, Jr., and H. S. Olcott. 1967. DDT residues in Pacific sea birds: a persistent insecticide in marine food chains. *Nature* 216: 589-591.
- Risebrough, R. W., R. J. Huggett, J. J. Griffin and E. D. Goldberg. 1968. Pesticides: Transatlantic movements in the Northeast Trades. Science 159: 1233-1236.
- Risebrough, R. W. 1969. Chlorinated hydrocarbons in marine ecosystems. In Chemical Fallout. Ed. M. W. Miller and G. G. Berg. Chas. C. Thomas Publ., U.S.A. pp. 5-23.
- SCEP, Report of the Study of Critical Environmental Problems. 1971. Man's Impact on the Global Environment. MIT Press, 319 pp.
- Smith, R. M. and C. F. Cole. 1971. Chlorinated hydrocarbon insecticide residues in winter flounder, *Pseudopleuronectis americanus*, from the Weiveantic River estuary, Massachusetts, J. Fish. Res. Bd. Canada 27: 2374-2380.
- Tarrant, K. R. and J. O. Tatton. 1968. Organochlorine pesticides in rainwater in the British Isles. Nature 219:725-727.
- Tatton, J. O. and J. H. A. Ruzicka. 1967. Organochlorine pesticides in Antarctica. Nature 215: 346-348.
- Wolman, A. A. and A. J. Wilson, Jr. 1970. Occurence of pesticides in whales. *Pesticide Monitoring J.* 4: 8-10.
- Wurster, C. F., Jr. and D. B. Wingate. 1968. DDT residues and declining reproduction in the Bermuda Petrel. *Science* 159: 979-981.