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DDT and Its Metabolites in Western Gull Eggs from Southern California and Northwestern Baja California

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Historically, islands off the Northwestern coast of Baja California hosted large breeding colonies of seabirds. Three decades ago DDT and DDE achieved such high levels in the region as to cause reproductive failure of brown pelicans (*Pelecanus occidentalis*; Jehl 1973, Anderson *et al.* 1975) and double-crested cormorants (*Phalacrocorax auritus*; Gress *et al.* 1973). In 1981-82 pintails (*Anas acuta*) collected in San Quintín, Baja California, and terns (*Sterna elegans* and *S. caspia*) at San Diego Bay still had detectable levels of pp'-DDE (Mora *et al.* 1987; Ohlendorf *et al.* 1985), but the mobility of these species did not allow for precise determination of the origin of the pesticides. Since the early 1970's the level of bioaccumulation of DDT and its metabolites in birds in Northwestern Mexico has been unknown.

To document the current accumulation of pesticide residues in the region, we decided to study a species that: (a) did not have any current conservation problems, (b) reproduced widely throughout the study area, and (c) whose eggs could be used to monitor local conditions. The Western gull is abundant in the region, has breeding colonies on many of the islands, and does not face any conservation problems. Individuals of this species remain near an area where food and breeding conditions are optimum (Spear 1988) and exhibit strong nesting-area and group fidelity (G. Hunt pers. comm. and L. Spear pers. comm.).

The objective of this work was to determine the concentration of DDT and its metabolites in eggs of Western Gulls (*L. occidentalis*), from the southern coast of California and the Northwestern coast of Baja California.

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MATERIALS AND METHODS

The study sites were distributed from North Island, San Diego Bay, California (32° 35' N, 117° 07' W) south to Isla San Martín, Baja California (30° 24' N, 115° 57' W; Figure 1). Within this area we selected four sites with Western Gull breeding colonies: North Island, Islas Los Coronados, Islas Todos Santos, and Isla San Martin. By using this north-south gradient we hoped to be able to analyze patterns in the accumulation of marine contaminants.

North Island is located in the center of San Diego Bay, and is primarily occupied by a U.S. Naval Air Station. Islas Los Coronados (32° 35' N, 117° 07' W) are located west of the Tijuana River Estuary, immediately south of the border between Mexico and the United States. They are 13 Km from the coast, and 38 Km south of North Island. They include four islands: two large ones in the north and south, and two small ones in the middle. The breeding colony sampled was on one of the latter, "Roca del Medio".

Islas Todos Santos (30°24' N, 115°57' W) are two islands separated by a deep and narrow submarine canyon in front of Bahía de Todos Santos (Ensenada Bay) and 5.5 Km northwest of Punta Banda. Within Bahía de Todos Santos lies Estero de Punta Banda, a coastal lagoon adjacent to the Maneadero farming area. Farming practiced here is cash-crop type with ample use of pesticides. Samples were taken from the southern island, the largest and steepest of the two.

Isla San Martín (30°24' N, 115°57' W) is a small volcanic cone 5 Km off the coast of San Quintín. The nearby coast is one of the important cash-crop farmlands of the state. Pesticides are widely used in it.

In May 1991 we collected 10 eggs from North Island, 21 from Islas Los Coronados, 23 from Islas Todos Santos, and 21 from Isla San Martin. All eggs were taken randomly, from different nests, individually wrapped in aluminum foil, immediately frozen, and kept so for five months, until their analysis. We measured length (L) and width (W) of each egg and extracted its contents. The eggshells were washed, dried and individually preserved in plastic bags; later they were sent to the Western Foundation of Vertebrate Zoology (Camarillo, California), where Lloyd F. Kiff and Clark Sumida measured their thickness to the nearest 0.001mm. Five thickness measurements for each egg were averaged. We determined amount of fat in each egg by extracting it with chloroform-methanol-water (Blight and Dyer 1959), and obtained percentage of water by drying 1g of sample at 70°C for 72 hours.

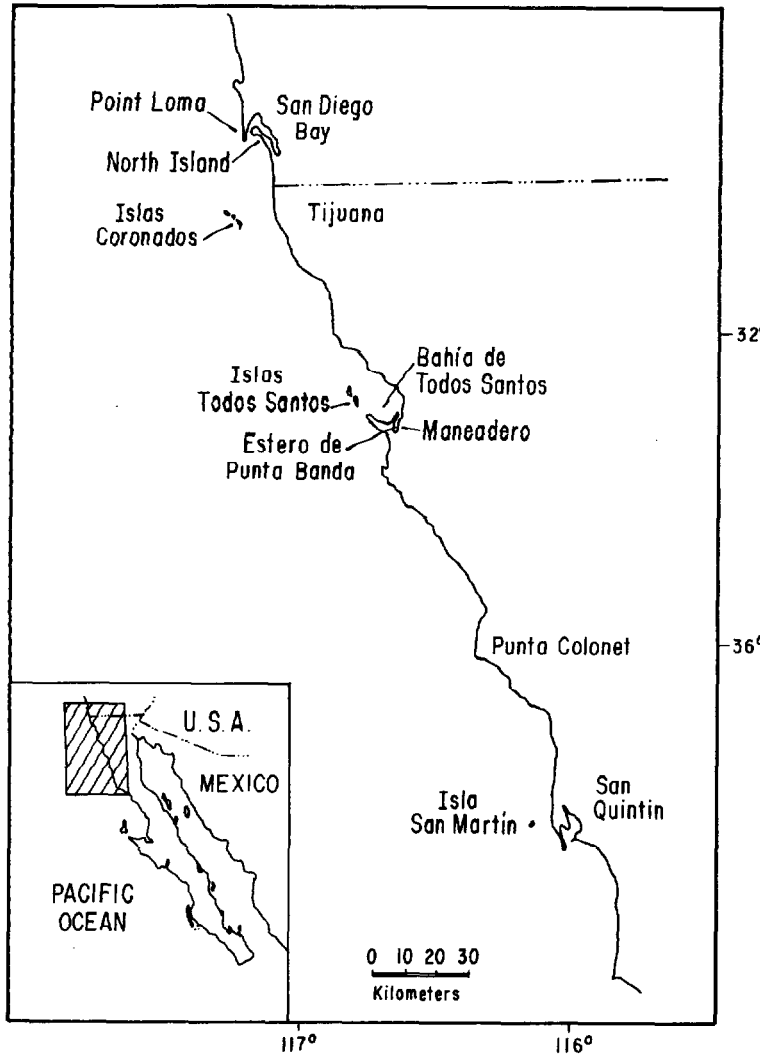

Figure 1. Study area and sampling sites.

To extract and quantify DDT and its metabolites we used a modification of Martin *et al.'s* (1980) technique. We dried 30 g of material with Na_2SO_4 and obtained an extract using acetonitrile under ultrasound for 10 minutes. This extract was transferred to petroleum ether, concentrated, and forced through a florisil column for cleanup. From this latter solution, we obtained two fractions: one using 100% petroleum ether, and the other using a solution of ethyl ether - 6% petroleum ether.

We analyzed the samples for pp'-DDT, pp'-DDE, pp'-DDD, op'- DDT, op'-DDE and op'-DDD. The values of pp'-DDT and pp'-DDD were added to avoid errors due to the conversion from the former to the latter during storage (Jefferies and Walker 1966). The Analyses were performed with a Hewlett-Packard 5890A gas chromatographer equipped with a Ni^{63} electron capture detector, a 7673A automatic injector and an HP 3396A integrator. To separate the pesticides we used J&W DB-5 capillary column of 30 m length and 0.32 mm diameter. Quantification of compounds was through direct calibration using standards from the U.S. Environmental Protection Agency (EPA). The lower limit of detection was ~1.00 ng g-1. Decachlorbiphenil was used as an internal standard to estimate percentage of recovery (range: 87 to 120%). Because of advanced embryonic development of some eggs, we corrected total concentration by $vol = 0.62LW^2$ (Anderson *et al.* 1970), assuming a specific gravity of 1.0 g cm^{-3} (Stickel *et al.* 1973).

We also collected all food residues from some nests on Todos Santos and San Martín Islands. Otholits in these residues were identified by Mark S. Lowry, at the Southwest Fisheries Science Center, La Jolla, California.

Concentrations of DDT and its metabolites were normalized by a $\log_{10}$ transformation. When the value of a pesticide residue in the sample was 0, it was substituted by 0.0005, half the detection limit of the analyzer, to allow for the transformation of the data. To analyze differences in concentration of metabolites between sites we used one-way analyses of variance (Zar 1974). When statistical differences were found, we used a Tuckey test to detect differences between particular means. We correlated eggshell thickness with concentration of pp'-DDE. All tests were performed with an $\alpha \leq .05$. However, in all cases where we detected statistical differences these had an $\alpha \leq .001$.

RESULTS AND DISCUSSION

pp'-DDE had the largest concentrations (96±4.06%; mean±standard deviation) of the total pesticide residues found and was present in all samples (Table 1). Overall pp'-DDE average was 3.5 μg g^{-1} and the maximum concentration 12.6 μg g^{-1}. No significant differences in concentration among the four sampling sites were found. op'-DDE was found at all sites, in 61% of the samples analyzed. The significant differences found (Table 1) show a loose N-S gradient in concentration.

That pp'-DDE makes up most of DDT-complex concentrations agrees with findings in similar studies (Gress *et al.* 1973, Jehl 1973, Ohlendorf

et al. 1985). The widespread presence of this compound in the region can be explained by the existence of a pp'-DDE pool adjacent to the California coast, that constantly recycles (Young et al. 1977), and was originated from the massive discharges of DDT that occurred in the past. The lack of significant differences among the study sites reflects the widespread existence of this compound.

pp'-DDT was found in 73% of the samples, while pp'-DDD was found in 29% of the samples. There were significant differences in the concentration of DDT (pp'-DDT + pp'-DDD; Table 1), Todos Santos and Coronados having the highest concentrations. op'-DDT was detected in 30% of the samples, in low concentrations (0.01-0.03 $\mu g\ g^{-1}$), not having differences between sites. op'-DDD was present in 39% of the samples with significant differences in concentration among sites, showing a N-S gradient (Table 1).

Table 1. Average concentrations of DDT and related compounds found in eggs of Western gulls in Northwestern Mexico and southwestern United States ($\mu g\ g^{-1}$, wet weight basis). Average fat content = 7.94%. Sites are arranged from north to south. Values in parenthesis indicate range of concentration values.

Compound	North Island N=10	Coronados N=21	Todos Santos N=23	San Martín N=21
pp'-DDE	3.7 (2.18~9.34)	4.23 (1.23~12.19)	2.55 (0.72~12.26)	3.39 (0.38~12.64)
op'-DDE	0.02 (0.003~0.06)	0.04 (0.01~0.12)	0.02 (0.005~0.06)	0.01 (0.006~0.06)
DDT[a]	0.07 (0.03~0.12)	0.09 (0.03~0.35)	0.14 (0.05~0.61)	0.04 (0.01~0.29)
op'-DDT	0.03 (0.02~0.05)	0.02 (0.003~0.05)	0.03 (0.006~0.07)	0.01 (0.003~0.02)
op'-DDD	0.02 (0.007~0.05)	0.007 (0.002~0.02)	0.009 (0.003~0.03)	0.007 (0.006~0.008)

[a] pp'-DDT + pp'-DDD (after Jeferies and Walker 1966).

The higher concentration of DDT in Todos Santos can be attributed to its proximity to the Maneadero agricultural area. This is consistent with pp'-DDT and op'-DDT found in mussels (*Mytillus edulis*) in nearby Estero de Punta Banda (Galindo-Bect and Flores-Báez 1991). Presence of op'-DDT suggests a recent of a commercial source of DDT (Lamont *et al.* 1970). Elsewhere the presence of DDT in birds has been associated with the use of *Kelthane®* (Mora *et al.* 1987). During 1991, 46'42l of *Kelthane®* were used in the state of Baja California (J. Contreras, pers. comm.). Whether this is the only local source of DDT remains to be determined.

Western Gull eggs from the California coast decreased from 0.413 mm thick in 1937 (Risebrough and Anderson in Hunt and Hunt 1973) to 0.376 mm in 1945 (L. Kiff pers. comm.). In 1972 eggshells of this species (Hunt and Hunt, 1973) were even thinner (0.334 mm) than in 1937 reflecting the DDT crisis in the Californias (Gress *et al.* 1973; Jehl 1973). Average thickness of our eggshells was 0.363 mm (range: 0.293-0.414; n=75). This value is 6% larger than that reported for 1972 and could be the result of the general reduction in the use of DDT. This increase is concordant with that found in the eggs of Brown Pelican (Anderson *et al.* 1975).

We did not find a significant correlation between eggshell thickness and concentrations of pp'-DDE (r=.19). This could be due to the moderate sensibility of Charadriiformes to pesticides (Peakall 1975). The negative correlation obtained by Hickey and Anderson (1968), in another species, was based on concentrations 7 times higher than those found by us.

Eggs from Isla San Martin had significantly thicker shells (0.380±0.022mm, mean±standard deviation; range: 0.358~0.402) than those from Islas Todos Santos (0.348±0.022mm; 0.326~0.370) and Islas Los Coronados (0.359±0.019; 0.340~0.378), while those of North Island (0.367±0.026; 0.341~0.392) were different from neither. These differences, in view of no differences in concentration of DDE among areas and the lack of a significant correlation between this compound and eggshell thickness, could be due to the type of food consumed. Feeding of gulls on clams or fish, which contain high levels of metabolizable calcium, favors the development of the eggshell (Pierotti and Annet 1990). Food leftovers collected from the nests showed that the gulls of Isla San Martín ate mainly fish while those at Todos Santos included many different items in their diet (including garbage). We have no data on the diet of Western Gulls on North Island and Islas Los Coronados, during the study.

Current concentrations of the DDT complex in Western gulls eggs from Islas Los Coronados and San Martín are much lower than those recorded in 1969 and 1970 for Brown Pelican (Anderson *et al.* 1975, Jehl 1973) and Double-Crested Cormorant eggs (Gress *et al.* 1973) from the same sites. Although Brown Pelicans (*Pelecanus occidentalis*), Double-crested Cormorants (*Phalacrocorax auritus*), and Western Gulls differ in feeding habits and sensibility to pesticides, the magnitude of the differences make these notewhorty. The current gull eggs from Isla San Martin had concentrations 1.7 times lower than those of pelican in 1970.

In general terms, concentrations of DDT and DDE are much lower today than they were in the 1960s and 1970s. This means that during the past 20 years the coastal marine ecosystem of Southern California and Northwestern Baja California has been recovering from the pesticide dumping prior to the 1960s. This fact is reflected in the thicker eggshells of Western gulls. However, the data suggests that some form of DDT pesticide might still be used, at least in Maneadero.

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