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Baseline

Organochlorine contaminants and maternal offloading in the lecithotrophic Pacific angel shark (*Squatina californica*) collected from southern California

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ABSTRACT

Pacific angel sharks (*Squatina californica*) are a benthic elasmobranch that occupy intermediate trophic level positions in coastal food webs. Angel sharks' life history characteristics make them susceptible to accumulating high amounts of contaminants. Four angel sharks were opportunistically captured in southern California and their liver and uterine contents were analyzed for PCBs, DDTs and other pesticides. High DDT:PCB ratios were found in the sharks indicating direct or indirect foraging near a local EPA Superfund Site. Organic contaminants were measured in ovulated eggs, indicating that females are able to maternally offload contaminants. Despite the potential mismatch between ovarian and uterine fecundity, we estimated females to offload approximately 13 ± 5% of their total body load, which represents the upper limit of this capability. Although low in sample size, the initial findings from this study suggest that habitat use might play an important role in contaminant accumulation in this species.

The Pacific angel shark (*Squatina californica*) is a benthic elasmobranch and one member of about 20 species of the family Squatinidae. Pacific angel shark habitat ranges on the continental shelf along the northeast Pacific Coast (Compagno et al., 2005). Sharks typically occupy depths of 1–200 m and can be found on muddy or soft bottom substrata where they can easily camouflage as they lie on the bottom. Members of the family Squatinidae have a unique feeding behavior characterized by lying still on the sea floor, making rapid lunges at passing prey (Fouts and Nelson, 1999), and using negative pressure to capture prey by sucking it into their mouths. Pacific angel sharks have been documented to feed on blacksmith (*Chromis punctipinnis*), queenfish (*Seriphus politus*), California corbina (*Menticirrhus undulatus*), and California halibut (*Paralichthys californicus*) making them one of the higher trophic level predators in coastal benthic ecosystems (Feder et al., 1974; Pittenger, 1984; Cortés, 1999). Although Pacific angel sharks have been documented to travel long distances (>7 km; Pittenger, 1984), angel sharks found around southern California's Channel Islands are genetically distinct, suggesting low dispersal (Gaida, 1997).

Pacific angel sharks have been targeted by gillnet fisheries in southern California for several decades (Richards, 1987; Holts, 1988) due to the relatively large numbers of fish that can be landed and the development of efficient at sea meat preparation and preservation procedures (Richards, 1987). Since the development of this fishery in the late 1970s, Pacific angel sharks were strongly targeted in southern California compared to other parts of its range (Holts, 1988) and currently no regulations on recreational catch limits exist for this species (CDFW, 2014). There is no longer a commercial fishery for this species, but it is occasionally taken as by catch in the California halibut fishery. However, little information exists about Pacific angel shark biology and ecology in southern California, which further complicates effective management.

Throughout southern California, and particularly around the Palos Verdes peninsula, high levels of legacy organic contaminants such as DDT (dichlorodiphenyltrichloroethane) and PCBs (polychlorinated biphenyls) can be found in marine biota at many trophic levels from forage fishes to marine mammals (Jarvis et al., 2007; Blasius and Goodmanlowe, 2008). DDT concentrations are proportionally high in biota from the Palos Verdes shelf due to the historic release of large amounts of contaminants in this area. Therefore, this unique DDT signature has been used as a general indicator of foraging proximity to this area (e.g. using [DDT]:[PCB] ratios; Krahn et al., 2007). For instance, DDT:PCB ratios for white croaker (*Genyonemus lineatus*) captured directly from the Superfund site were between 15 and 22 (Gossett et al., 1983), whereas coastal young-of-the-year white sharks (*Carcharodon carcharias*) caught throughout southern California

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were found to have ratios 5.21 ± 1.2 (Lyons et al., 2013). Blubber from local pinniped pups in southern California were found to have ratios approximately between 6 and 10 for species who's mothers were more resident (i.e. harbor seals *Phoca vitulina* and sea lions *Zalophus californianus*) while ratios were much less (~3) for northern elephant seals (*Mirounga angustirostris*), which spend considerable time offshore (Blasius and Goodmanlowe, 2008).

Due to their trophic position and potential longevity (Cailliet et al., 1992), Pacific angel sharks would be presumed to be susceptible to accumulating high levels of organic contaminants. However, no previous studies have examined legacy organic contaminants in this species. Since Pacific angel sharks are a relatively difficult to study species, gathering information whenever opportunities present themselves becomes important. Fortuitous collection of four Pacific angel shark specimens allowed for the examination of organic contaminants in two tissue types. The objective of this study was to provide baseline data for organic contaminant accumulation as well as document maternal contaminant offloading in this species.

In January 2010 and May 2014, one unsexed and three mature female Pacific angel sharks were opportunistically collected, respectively (Fig. 1). The unsexed shark (Angel-4) was donated from a local commercial gillnet fishery that operates off the Ventura flats in the northern region of southern California. A collaborator was able to collect samples of liver tissue from this shark. The three mature female sharks were collected from a local fish die off in the Marina Del Rey Harbor, just north of the Los Angeles Airport in Santa Monica Bay. Whole sharks were brought back to the CSULB Shark Lab and necropsied. Upon dissection, the three mature females were found to have ovulated eggs in both uteri. One of the females (Angel-1) had early stage embryos, while embryos were not visible in the yolky contents of the other two fish (Angel-2 and 3). Total weight of the yolky uterine contents was weighed and homogenized for each female.

Subsamples of liver (~1 g) and homogenized uterine contents (~3.5 g) were spiked with recovery surrogates (TCMX, PCB 30, 112, and 198; target recovery of 70–130%) prior to extraction on a Soxhlet apparatus. Samples were extracted with 200 mL of methylene chloride solvent for 14–16 h. After extraction, samples were concentrated and lipid content was determined gravimetrically by splitting the sample. Extracts were then cleaned up by elution through an Alumina-B/Silica gel with hexane, 30% methylene chloride (DCM) in n-hexane, and DCM and concentrated. Samples were transferred to autosampler vials and spiked with internal standards (4,4′-Dibromobiphenyl and 2,2′,5,5′-Tetrabromobiphenyl) prior to injection onto an Agilent gas chromatograph (GC; 6890N series) equipped with a mass selective detector (MSD; Agilent 5973 inert series). The GC column employed was a ZB-5 (Phenomenex; Torrance, California) fused silica capillary (0.25 mm ID × 60 m) with 0.25 μm film thickness. The temperature profile of the GC oven was programmed from 45 °C to 125 °C at 20 °C/min, then to 295 °C at 2.5 °C/min and held for 10 min. Injector and transfer line temperatures were set at 285 °C and 300 °C, respectively. The source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. Helium was used as the carrier gas at a flow velocity of 40 cm/s. The MSD was operated in the Electron Ionization (EI) mode and scanned from 45 to 500 amu at a rate of 1.66 scans/s. Concentrations of organic contaminants were quantified using the software in the GCMS system (Agilent Technologies) and reported on a wet weight (“ww”) basis. Measured contaminants were then categorized into groups: polychlorinated biphenyls (PCBs), DDT and four metabolite compounds (DDTs), and non-DDT pesticides. Total organochlorine concentrations were

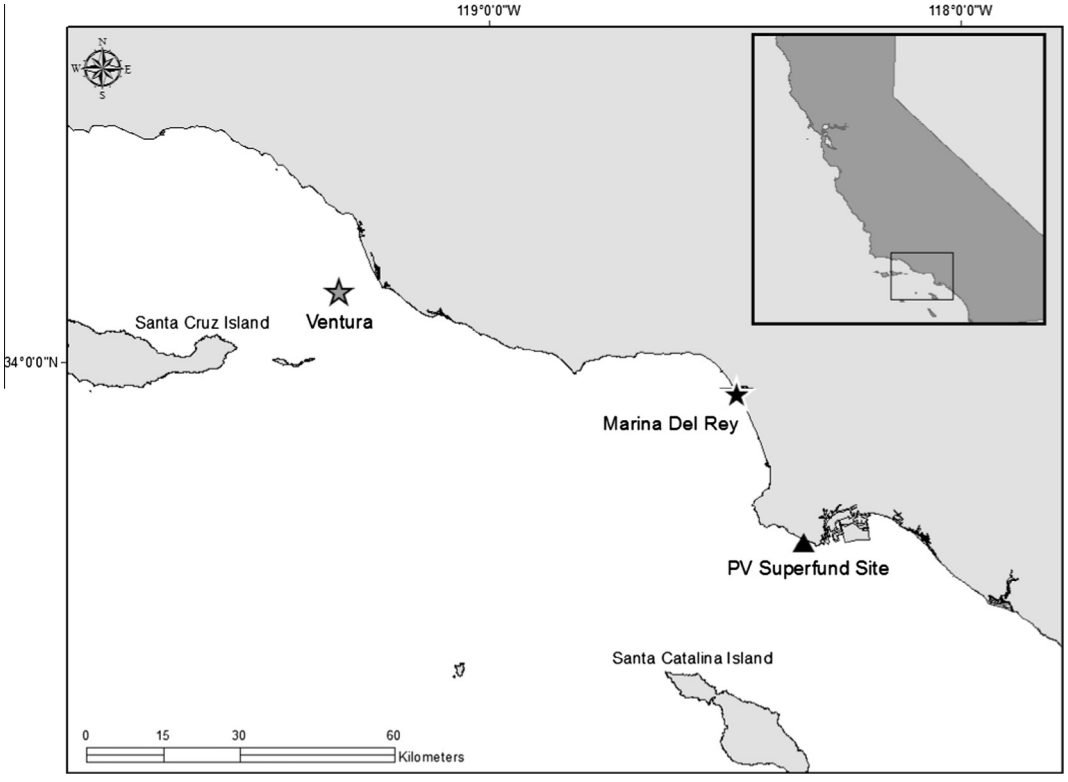

Fig. 1. Capture locations of angel sharks in southern California in proximity to the EPA Superfund site at Palos Verdes (black triangle). Pregnant females were sampled from in Marina Del Rey (black star) and the unsexed angel shark was sampled from Ventura (grey star).

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