

# **2007 Channel Islands Peregrine Falcon Study**

## **Final Report**



### **Prepared by:**

Brian C. Latta, The Bird Group  
230 Ross Street, Santa Cruz, CA 95060  
[blatta333@gmail.com](mailto:blatta333@gmail.com)

# **2007 Channel Islands Peregrine Falcon Study**

## **Final Report**

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U.S. Fish and Wildlife Service  
6016 Hidden Valley Road  
Carlsbad, CA 92001

**Submitted by:**

Brian C. Latta, The Bird Group  
230 Ross Street, Santa Cruz, CA 95060  
[blatta333@gmail.com](mailto:blatta333@gmail.com)  
on behalf of  
Santa Cruz Predatory Bird Research Group  
UC Santa Cruz Long Marine Lab  
Santa Cruz, CA 95060  
Brian J. Walton, Principal Investigator (Deceased 2007)

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This report is dedicated to the memories of Brian J. Walton, Scott H. Francis, and Daniel Brimm, who devoted the majority of their lives to realizing a successful recovery of the peregrine falcon in California.

## Table of Contents

INTRODUCTION	1
History	2
Permits	3
METHODS	3
Surveys	4
Boat Surveys	4
Ground Surveys	4
Classification of Peregrine Falcon Territories	4
Nest Monitoring	5
Breeding Chronology	5
Location of Nest Cliff and Eyrie (nest ledge)	6
Reproductive Success/Failure	6
Number of Young Produced	6
Banding and Sample Collection	6
Banding	6
Sample Collection	7
Nest Enhancement	8
Sample Analysis	8
Eggshell Measurement	8
Contaminant Analysis	9
Prey Remains	9
RESULTS	10
Surveys	10
Nest Monitoring	13
Breeding Chronology	13
Reproductive Success/Failure	13
Banding and Sample Collection	14
Sample Analysis	16
Eggshell Measurements	16
Contaminant Analysis	18
Prey Remains	20
DISCUSSION	24
Surveys	24
Monitoring	27
Reproductive Success and Eggshell Thinning	28
Addled Eggs	31
Contaminant Levels and Eggshell Thinning	32
Prey Remains and Eggshell Thinning	34
CONCLUSIONS	38
RECOMMENDATIONS	39
REFERENCES	40
APPENDICES	43

## List of Tables

Table 1. Territory Status by Island.	11
Table 2. Status, Reproductive Outcome and Young Produced by Territory.	12
Table 3. Breeding Chronologies by Territory.	13
Table 4. Breeding Status and Reproductive Outcome by Island.	14
Table 5. Chicks Banded by Territory.	15
Table 6. Samples Collected by Island.	15
Table 7. Breeding Territory and Natal Origin of Two Resident Adult Females.	15
Table 8. Eggshell Measurements of 2007 Samples.	16
Table 9. Eggshell Measurements of 1988-2006 Channel Islands Samples	17
Table 10. Levels of DDTs and PCBs in four peregrine falcon eggs collected in 2007	19
Table 11. 2007 Prey Items Collected (MNI) by Island.	20
Table 12. MNI, Total and Percent Biomass of 2007 Prey Items by Species.	23
Table 13. MNI, Total Biomass, and Percent Biomass of Prey Items by Habitat Type for Islands Combined.	24
Table 14. Natal Origin of Adult Breeding Peregrine Falcons Captured on the Channel Islands from 1992 - 2007.	28
Table 15. Eggshell Thinning, DDE and PCB wet weight values ( $\mu\text{g/kg}$ ) for 4 Channel Islands Peregrine eggs collected in 2007.	33
Table 16. Eggshell Thinning compared to Percentage of Biomass of Spring Diet by Island in 2007.	36

## List of Figures

Figure 1. The California Channel Islands and southern California Coast.	1
Figure 2. J. Pagel Collecting Eggshell Fragments from SRI Lime Pt. Alternate (Lobos Cyn) Peregrine Eyrie.	7
Figure 3. Prey remains (feathers) and Peregrine Nestlings in 2007 Santa Barbara Island Eyrie.	8
Figure 4. Peregrine Falcon Territories on the Northern Channel Islands.	10
Figure 5. Peregrine Falcon Territories on the Southern Channel Islands.	11
Figure 6. Percent Biomass by Habitat Type of Prey Remains collected on the Channel Islands in 2007.	22
Figure 7. Percent MNI by Habitat Type of Prey Remains collected on the Channel Islands in 2007.	22
Figure 8. California vs. Channel Islands Peregrine Population Recovery.	25
Figure 9. Newly hatched Peregrine Falcon Nestlings and unhatched egg in 2007 Santa Barbara Island Eyrie.	26
Figure 10. Channel Islands Peregrine Population Recovery.	27
Figure 11. Percent Eggshell Thinning 1988-2007.	29
Figure 12. Average Eggshell Thinning by Island from 1988-2007.	30
Figure 13. Average Eggshell Thinning by Island for 2007.	30
Figure 14. Comparison of Eggshell Thinning v. Reproductive Failure on San Miguel, Santa Rosa, and Santa Cruz Islands 2007.	31
Figure 15. Buddy™ Digital Egg Monitor with peregrine falcon egg from SMI Carbon Point.	32

Figure 16. Buddy™ Digital Readout of Live Peregrine Falcon Egg from SMI Carbon Point.	32
Figure 17. Western gull partially consumed by a Peregrine Falcon on Santa Barbara Island in 2007.	35
Figure 18. Percent Biomass per Habitat Type of the 2007 Spring Diet by Island.	36

## INTRODUCTION

From the beginning of its widespread use as a pesticide in the 1940s until 1971, an estimated 2,000 metric tons of the organochlorine compound DDT (dichlorodiphenyltrichloroethane) and its derivatives were discharged into the wastewater system of the Los Angeles County Sanitation District from a Torrance, California manufacturing plant operated by the Montrose Chemical Corporation. An estimated 100 metric tons of DDT remain deposited in the sediments of the relatively shallow Palos Verdes Shelf in the Pacific Ocean southwest of Los Angeles, subject to upwelling and circulation throughout the California Channel Islands archipelago by the seasonally shifting currents of the San Pedro and Santa Barbara Channels (Figure 1).

**Figure 1. The California Channel Islands and southern California Coast.**



The environmental impact of this monumental contamination included the extirpation of apex avian predators, such as American peregrine falcons (*Falco peregrinus anatum*) and bald eagles (*Haliaeetus leucocephalus*) that feed at the top of the marine food chain, from the California Channel Islands by 1960. The continuing presence of DDT and its metabolites in the marine ecosystem greatly hindered the extensive peregrine falcon and bald eagle restoration efforts, begun in the late 1970s and early 1980s respectively, by negatively affecting reproductive success of those species on the islands.

In 1990, the United States Department of Justice filed suit against Montrose Chemical Corporation and others under the federal Superfund law. The claims were settled in 2001 and over \$140 million was paid by the defendants to be used for studies, restoration, and clean-up. Funding for this 2007 study of peregrine falcons on the Channel Islands resulted from that settlement and is administered by the Trustee Council of the Montrose Settlements Restoration Program.

## History

Through the interpretation of historical records, field notes, and documentation associated with egg collections, the subpopulation of American peregrine falcons breeding on the Channel Islands of Southern California and Mexico's Coronados Islands, just south of San Diego, has been estimated at 20 pairs prior to the 1940s (Kiff 1980). The documentation suggests that the peregrine falcon may have been resident on each of the eight Channel Islands during the breeding season, with the maximum number of documented active territories on those islands (excluding the Coronados Islands) estimated to be 15-16 (Kiff 2000). Kiff (1980, 2000) notes that, due to the lack of comprehensive surveys, this figure should be considered a low end estimate rather than a reflection of the true size of the historical population.

Prior to the mid 1940s, the peregrine falcon was considered a fairly common year-round resident on the Channel Islands and the southern California mainland with a stable population (Willett 1912, Howell 1917, Grinnell and Miller 1944). However, as occurred in most of North America, the introduction of the organochlorine pesticide, DDT, into the environment caused peregrine falcons and other avian species to lay eggs with thinner shells, retarding reproduction, which brought about a steep decline in the peregrine population in California (Anderson and Hickey 1972, Herman *et al.* 1970, Herman 1971, Peakall 1974, Thelander 1976, 1977). According to Kiff (1980, 2000), peregrines had been extirpated from the Channel Islands as a breeding species by the mid 1950s. Subsequently, very few records of single peregrines and no records of pairs on the Channel Islands have been found for the period between 1949 and the late 1980s (Hunt 1994).

In a survey of 62 historical California nest sites in 1970, a low of two known nesting pairs were found along with two other territories occupied by single individuals (Herman 1971). In 1977, the Santa Cruz Predatory Bird Research Group (SCPBRG) began a program of releasing captive-bred and captive-hatched peregrines throughout California and neighboring states. As part of this program, peregrine falcon eggs were removed from nest sites with high eggshell thinning levels, hatched in a laboratory, and chicks were released through nest site manipulation or hacking (Walton and Thelander 1985). By 2007, SCPBRG had released over 1,000 peregrine falcons into the region, including 37 on the Channel Islands (12 on San Miguel, 17 on Catalina, 4 on Santa Rosa, and 4 on Santa Cruz) as well as scores of birds on the mainland coast within 100 miles of the islands (TBG unpublished data). In 1985, three male peregrines were released wearing blue USGS bands at the Cuyler Harbor hack site on San Miguel Island. In 1986, one of these birds, then a 1 year-old male (USGS band # 816-643353), and a 1 year-old un-banded female from the mainland became the first pair re-established to the islands, at San Miguel's Hoffman Pt. (TBG unpublished data). The pair laid their first clutch of eggs in 1987 which failed to hatch. Despite that outcome, this milestone marked the first step on the road to recovery of the peregrine falcon on the Channel Islands.

From 1992 to 1994, Dr. Grainger Hunt (then at SCPBRG) led field investigations of peregrines on the Channel Islands, as part of the evidence gathering phase of the United States, *et al.* v. Montrose Chemical Corporation of California, *et al.* case. These investigations were in coordination with SCPBRG's ongoing management and monitoring of the recovering California peregrine falcon population (Hunt 1994, SCPBRG unpublished data). Hunt (1994) documented nine active peregrine territories on the four northern Channel Islands. These investigations



## 2007 Channel Islands Peregrine Falcon Study Final Report

focused on winter (pre-egg laying) diet and collection of addled eggs, eggshell fragments, prey remains, and whole prey for an analysis of eggshell thinning and DDE (metabolite of DDT) contamination of both peregrine eggs and prey species. Hunt (1994) concluded that breeding peregrine falcons on the Channel Islands were still consuming large amounts of DDE in their diet. He collected a number of non-migratory seabirds on the islands in 1992 and 1993, identified as major constituents of the resident peregrine falcon diet through prey remains analysis, and found that they contained DDE levels that were elevated enough to be the likely cause (through bioaccumulation) of the high degree of thinning and DDE contamination in the peregrine eggs they examined.

From a low of two nesting pairs found in a survey of 62 historical California nest sites in 1970 (Herman 1971), the state-wide peregrine falcon population size rose to an estimated 220+ pairs by 2006 (TBG unpublished data). The continued persistence of DDT and its metabolite, DDE, however, slowed the recovery process and continues to affect peregrine falcon reproduction especially in coastal California and the Channel Islands. While the number of active territories (occupied by a breeding pair) on the Channel Islands continues to increase, recruitment from mainland sources (i.e. SCPBRG releases and wild eyries), is still apparent, as indicated by the observation of banded birds whose natal origin is the mainland.

The goal of this 2007 study was to assess the current status of peregrine falcons on the Channel Islands and the on-going effects from DDT contamination.

### **Permits**

The American peregrine falcon is protected by the federal Migratory Bird Treaty Act, the California Endangered Species Act, and is on the California Fully Protected List. The peregrine falcon was removed from the Federal List of Endangered Species in 1999. This study was conducted on public lands managed by the Channel Islands National Park, Channel Islands National Marine Sanctuary, United States Navy, and private lands managed by The Nature Conservancy, Catalina Island Conservancy, the UC Santa Barbara Natural Reserve System, and the University of Southern California Wrigley Marine Science Center. This study was conducted by SCPBRG under the following permits:

USGS Federal Bird Banding Permits 22383 and 23395

Federal Migratory Bird Salvage Permit

CDF&G Memorandum of Understanding (MOU) for peregrine falcon studies

CDF&G Scientific Collecting Permits SC-001547 and SC-007993

USDI-NPS Scientific Research and Collecting Permit #CHIS-2007-SCI-0001

Channel Islands National Marine Sanctuary Research Permit #CINMS-2007-001

Catalina Island Conservancy Scientific Research Permit #07-01

Approved Protocols from the U.C. Santa Barbara Institutional Animal Care and Use Committee (IACUC) and U.C. Santa Cruz Chancellor's Animal Research Committee (CARC)

## **METHODS**

### **Surveys**

SCPBRG raptor biologists conducted surveys from boats or on foot of known nesting territories and potential nesting territories to determine the presence or absence of peregrine falcons. Survey routes and locations were based on prior knowledge of the known and potential peregrine nesting habitat of the islands, reported peregrine sightings from knowledgeable non-SCPBRG observers, and from interpretation of topographic maps. We conducted initial surveys prior to the last week of February 2007, which is the earliest known onset of egg-laying in California. Additional surveys of vacant and potential territories continued through March. We also conducted follow-up observations at potential nest cliffs in response to peregrine falcon sightings by non-SCPBRG personnel on an opportunistic basis throughout the study. We followed up survey observations of peregrines in known and newly confirmed territories with scheduled nest monitoring observations.

### **Boat Surveys**

SCPBRG biologists conducted surveys of coastal cliffs of some islands (i.e., Santa Cruz, Anacapa, Santa Catalina) from watercraft. We scanned and observed the cliffs with 10 x 40 binoculars while drifting or at anchor from a moderate distance (~400 m) and close up (<100 m). We scanned the skylines and likely perch spots for perched peregrines and looked for specific types of bird droppings (whitewash) attributable to large falcons that may indicate recent residency. We watched for flying falcons and listened for falcon vocalizations. We also employed homing pigeons as a survey tool at Santa Catalina Island, a technique used successfully by Hunt (1994) on the northern islands. We released single homing pigeons from the vessel at a distance of from 500 to 1,000 meters from potential nest cliffs in order to elicit pursuit responses from perched peregrines that may have been hidden from view. We then followed the pigeon towards the cliffs with the boat and tracked it visually until it landed on the island, flew out of sight or was pursued by a peregrine. At known nest cliffs we anchored the boat and observed for periods of up to 6 hours at a distance that gave the widest panoramic view of the cliff but was close enough to allow observers to hear peregrine vocalizations and observe perched and/or flying birds.

### **Ground Surveys**

Ground surveys of known and potential peregrine territories consisted of observing the cliffs using 10 x 40 binoculars and 20-60x zoom spotting scopes from optimal observation points (OPs) for up to 6 hours per visit. An optimal OP provided the observer the best possible view of the cliff face at distances from 150 to 1,000 meters. During observation periods, SCPBRG biologists scanned the skylines and perch spots for perched falcons, looked for falcon whitewash, watched for flying falcons, and listened for falcon vocalizations. At known territories, if peregrines were not detected after 4 hours of observation at their primary nest cliff, we surveyed other potential cliffs nearby to determine if the pair was using an alternate nest cliff. Some pairs move to an alternate nest cliff within their territory if there was a mate replacement and/or if they have failed in the previous year's nesting attempt.

### **Classification of Peregrine Falcon Territories**

We classified peregrine falcon territories into the following categories:

Active - contained a resident pair throughout the breeding season and a breeding attempt was documented.

Transitional - contained a new or immature pair member and no breeding attempt was observed.

Occupied - contained one resident falcon throughout the breeding season.

Inactive - was known to have been active at least once from 1984 to the present, but was vacant during the 2007 breeding season.

Wintering - contained one or more transient peregrines that left by mid-April.

Unconfirmed - unsubstantiated reports from non-SCPBRG personnel of a pair or single peregrine residing at a cliff throughout the breeding season.

Potential - appeared to have been suitable for breeding but was vacant and was not known to have ever been confirmed or historic.

It is possible for some territories to exhibit more than one classification in a given year. For example, a lone resident in an occupied territory may form a loose pair bond with a wintering transient (Occupied/Wintering Territory) who then leaves in the spring and is replaced by a floater (non-territorial peregrine). If a new pair bond is formed but no breeding is attempted the territory is then considered transitional.

### **Nest Monitoring**

SCPBRG biologists monitored active peregrine territories to determine breeding chronology, location of nest cliff and eyrie (nest ledge), egg laying and incubation periods, reproductive success/failure, recycling attempts, and number of young produced. We used 10 x 40 binoculars and 20x-60x zoom spotting scopes to observe peregrine behavior from optimal OPs (see Ground Surveys above) for periods of up to ten hours. We returned to nest sites at intervals of one day to two weeks between visits, depending on weather and logistics. We also monitored occupied territories throughout the breeding season to determine whether the single occupants had acquired mates.

### **Breeding Chronology**

The breeding chronology is the temporal progression of behaviors and actions of a breeding pair of peregrines through the breeding season from courtship to the dispersal of young. Accurate determination of the dates of certain phases of the breeding chronology (e.g., egg laying, onset of hard incubation, and hatching) was crucial for the timing of nest entries for sample collection and chick banding to minimize exposure of eggs and chicks to the elements and reduce the potential for premature chick fledging during the climbs.

Where we could see into the nest ledge from the OP (N=12), we determined the different stages of the breeding chronology by observing the behavior of the birds, presence of eggs, and feeding of young on and around the nest ledge. Where the nest ledge was not visible from the OP (N=13), we determined the breeding chronologies through interpretation of the behaviors of the breeding pairs on or around the nest cliffs. See Appendix i for description of peregrine breeding

behaviors. Determining the accuracy of the nesting chronologies varied per the skill level of the observer, and ranged from 0 to +/- 4 days.

### **Location of Nest Cliff and Eyrie (nest ledge)**

Where possible, we located probable nest cliffs and eyries by determining the focal points of the peregrine pairs' courtship behaviors which included single and mutual ledge displays. We determined eyrie location on the nest cliff by either directly observing eggs or incubating falcons from the OP or, in most cases, by repeated observations of the general location on the cliff that pair members went to and came from during successive incubation exchanges and the flight vectors of ingressing and egressing pair members during those exchanges. On Santa Cruz Island, we used a helicopter to locate the eyrie at Bowen Point and a boat to locate the Arch Rock eyrie, neither of which could be observed from land.

### **Reproductive Success/Failure**

SCPBRG biologists determined that a full clutch of eggs had been laid either by direct observation of eggs in the nest from the OP, or by observing a change in pair behavior wherein incubation exchanges became more regular (i.e., every 2-4 hours) and neither the eggs nor the eyrie was left unattended for more than 10 minutes. We refer to this stage of the chronology as "hard incubation" which generally begins after the laying of the third or fourth egg. Peregrine falcons typically lay two to four eggs per clutch. We determined reproductive success by direct observation of young in the nest or by the repeated observations of food being carried into the eyrie by one or both adults.

SCPBRG biologists determined reproductive failure by documenting either: 1) an abrupt cessation of regular incubation exchanges prior to expected hatching (ca. 33 days after onset of hard incubation), which was sometimes accompanied by resumption of pre-egg laying courtship behaviors (i.e., ledge displays, copulation), or 2) a gradual cessation of incubation exchanges and then loss of interest in the eggs and abandonment of the eyrie after the expected hatching date, or 3) the apparent failure of a courting adult pair to ever reach the hard incubation stage (i.e., breaking eggs during laying).

### **Number of Young Produced**

We determined the number of young produced by direct observation of young in the nest from the OP, by entering the nest to band young, or by direct observation of unbanded young at the nest cliff shortly after fledging.

### **Banding and Sample Collection**

For chick banding and sample collection Brian Latta (SCPBRG) and Dr. Joel E. Pagel (USFWS and SCPBRG research affiliate) used standard technical rock climbing techniques, rappelling from the top of the cliff to enter nest ledges (Pagel and Thorstrom 2008). We trapped select adult peregrine falcons near the nest cliff for band identification and sample collection using a dho gazza net set (Bloom et al. 2007) and a live great horned owl (*Bubo virginianus*) lure.

### **Banding**

Using standard peregrine falcon nest entry methods, Latta or Pagel banded chicks in the nest when they were approximately 17 to 25 days old. We placed USGS lock-on bands on one leg and black alpha-numeric visual identification (VID) bands (ACRAFT Sign and Nameplate Company Ltd., Edmonton, Alberta, CA) on the opposite leg. We sexed chicks by tarsi width. Females were banded with size 7a bands and males size 6.

### **Sample Collection**

We collected eggshells, eggshell fragments, addled (dead or infertile) eggs, and/or prey remains from every 2007 peregrine nest ledge we determined safe to enter (n=18). We also collected eggshell fragments, addled eggs, and prey remains from some eyries where we had observed peregrines nesting between 2001 and 2006, and analyzed some Channel Islands samples collected and curated in prior years (i.e., 1995-2006). We used tweezers to pick up eggshell fragments from the surface of the nest substrate and then used a 1/8 inch screen kitchen sieve to sift fragments from the scrape (nest cup) and surrounding substrate (Figure 2). We placed the fragments in I-chem glass sample jars for eggshell thickness analysis by Sam Sumida. Samples were curated at the Western Foundation of Vertebrate Zoology (WVZ) in Camarillo, California.

**Figure 2. J. Pagel Collecting Eggshell Fragments from SRI Lime Pt. Alternate (Lobos Cyn) Peregrine Eyrie. (photo B. Latta)**



We entered three peregrine nests (East Anacapa, Santa Barbara Is., SMI Carbon Pt.) after approximately 21 days of incubation to check egg viability using a portable digital egg monitor (Buddy™, Avitronics, Cornwall, UK) and to collect non-viable eggs before they broke (see Appendix iii. Protocol for Use of a Digital Egg Monitor for Collecting, Preparing, and Shipping Egg Samples from the 2007 Channel Islands Peregrine Falcon Monitoring Effort). All addled

eggs collected in the field were transferred to the USFWS Carlsbad Office where Dr. Pagel and Dr. Katie Zeeman (USFWS) prepared them for analysis following the USFWS protocol. We collected the feather and bone remains and regurgitated pellets of prey species from peregrine nest ledges (Figure 3) and placed them into labeled zip-loc bags for later identification by N. John Schmitt at the WFVZ.

**Figure 3. Prey remains (feathers) and Peregrine Nestlings in 2007 Santa Barbara Island Eyrie. (photo B. Latta).**



We used a great horned owl (*Bubo virginianus*) and a dho-gazza net set (Bloom 1987) to attempt capture of resident adult peregrines at three territories during the chick-rearing period. We took biometric measurements, recorded band numbers, and collected 2.0 ml of blood from the brachial vein. We transferred the blood to sterile cryovials (Nalgene) and refrigerated them as quickly as possible.

### **Nest Enhancement**

In almost every case, Latta or Pagel enhanced or reconditioned existing nest ledges to some degree. Enhancement/reconditioning methods ranged from simply removing sharp rocks and leveling out the existing substrate to building up the edges of sloping ledges with nearby rocks and/or adding additional native substrate to stabilize and/or slightly increase the size of the ledge floor. The goal of these enhancements was to decrease the chance of future egg breakage. Additionally, by smoothing out the substrate and old scrapes (nest cups) we assure that future eggshell fragment samples collected will represent clutches laid after 2007.

### **Sample Analysis**

#### **Eggshell Measurement**

Clark "Sam" Sumida measured the eggshell and eggshell fragment samples to the nearest 0.001 mm using a Federal model P61 dial indicator mounted on a Federal model 35B-21 comparator

stand. Prior to measurement he examined the interior and exterior surfaces of each fragment at 4.8x and/or 8x using a Lomo SF-100 Binocular Stereo Microscope (MBC-10) and separated out any non-peregrine falcon fragments. For whole hatched and opened eggshells he took measurements at ten different locations at or near the equator of the lower portion and in one case ten measurements around the perimeter of the cap for "with membrane" data. For fragment samples he measured 10 or more chosen at random from each sample. He measured all of the fragments in the few samples that contained less than 10 fragments. Samples were measured both without, and when present, with the eggshell membrane. He adjusted the values for samples without membrane by adding the standard peregrine eggshell membrane thickness value (0.063) to achieve comparable eggshell thickness values. We then derived a Clutch Mean value by taking the geometric mean of the measurements of the all of eggshells and eggshell fragments collected that represented each individual clutch of eggs. We converted the clutch means (thickness) values to a Percent Thinning value with the equation  $N\% = [1 - (\text{thickness}/0.364)] \times 100$ , using 0.364 mm as the standard pre-DDT California eggshell thickness derived from the mean of measurements of 573 California peregrine eggshells collected prior to 1947 (Kiff 1994).

### **Contaminant Analysis**

SCPBRG and the USFWS sent egg contents and whole blood samples to Alpha Analytical, Incorporated (320 Forbes Boulevard, Mansfield, MA 02048). Samples were analyzed for percent lipids, percent solids, concentrations of DDT isomers and polychlorinated biphenyls (PCBs). Contaminant levels were determined using USEPA standard method 8270 with modifications for extraction and quantification of PCBs as single congeners, homologs and / or commercial aroclors as well as pesticides using gas chromatography/mass spectrometry with selective ion monitoring (GC/MS-SIM). Details of analytical methods are provided in Alpha Analytical, Inc. technical standard operating procedure number SOP-O/015 (see Appendix vi).

Specifically, samples were analyzed for o,p'- and p,p'- isomers of DDT and its metabolites (DDE and DDD), 47 out of 209 individual PCB congeners, and the ten homolog classes (monochloro- decachlorobiphenyl). The target PCB congeners, as designated by their International Union of Pure and Applied Chemists (IUPAC) numbers included those that are typically dominant in avian samples (i.e., PCB numbers 153, 138, 180, 118, 99, 105, 187, 170 and 31), congeners representing 9 of the 10 possible homolog classes (Cl<sub>2</sub>-Cl<sub>10</sub>), and non-ortho-PCB congeners recognized for their dioxin-like toxicity (Van den Berg et al. 1998,) most notably PCBs 77, 81, 126 and 169.

### **Prey Remains**

N. John Schmitt identified and quantified the prey remains. First he compared individual feathers and other body parts to a reference collection to key them out to species or genus. He then used duplicate feathers or body parts (e.g., two or more left #1 primary remidges, two or more right feet) to determine minimum number of individuals (MNI) per sample from each eyrie. We used published body mass data to determine biomass for each species (Dunning 1993). In cases of sexual dimorphism in a species we used the average mass of the male and female. When prey items could be keyed only to genus we used the average mass of the species of that genus likely to appear on the islands in spring. We then assigned prey items to the categories of Land birds, Shorebirds, or Sea birds, depending on where they primarily foraged while on or around the Channel Islands, in order to look at the relative contribution from each corresponding ecosystem to the nesting season diet.

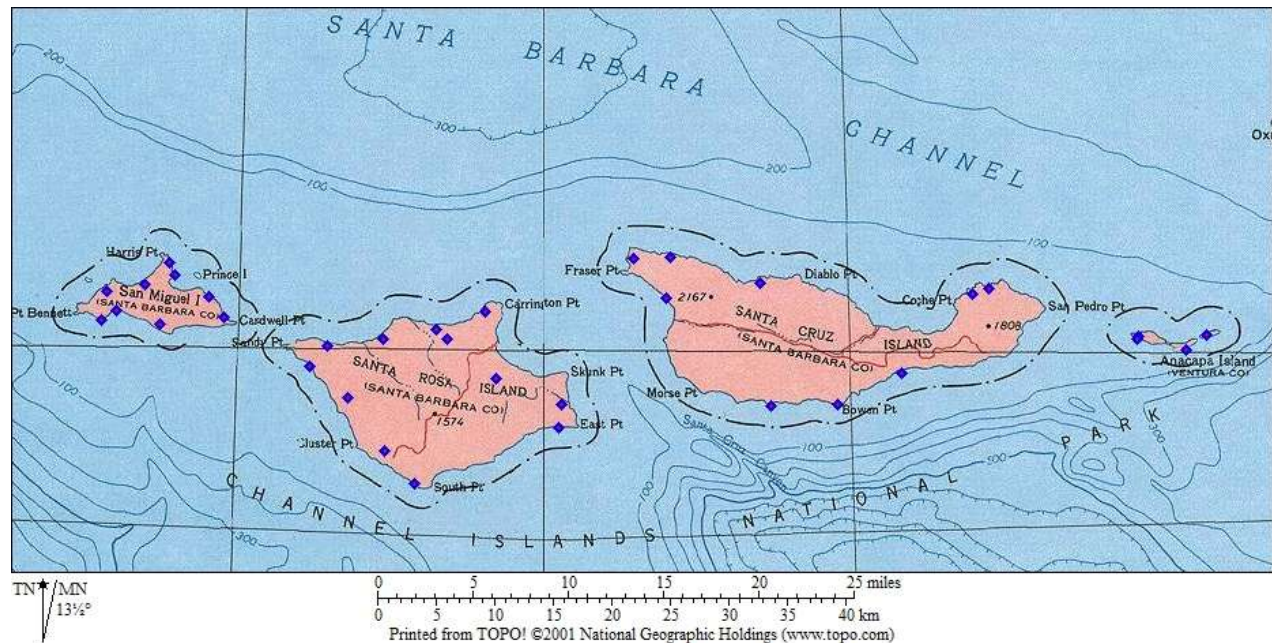


## RESULTS

### Surveys

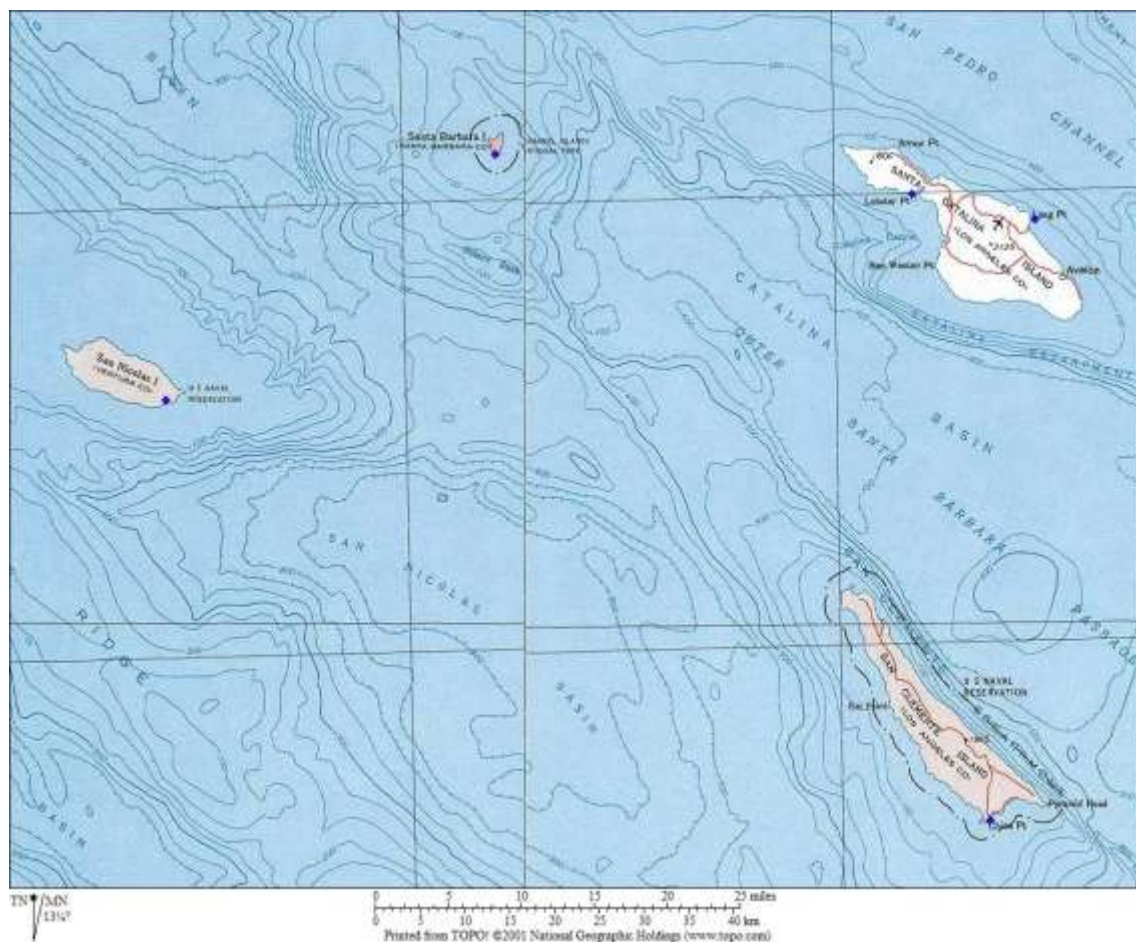
We visited all eight Channel Islands and documented the status of 35 peregrine falcon territories (Figures 4 and 5, Table 1). Twenty-five territories (71.4%) were active with resident breeding pairs (San Miguel=7, Santa Rosa=8, Santa Cruz=7, Anacapa=2, Santa Barbara Island=1). Two territories (5.7%) were transitional, each with a sub-adult pair member (Santa Cruz=1, San Nicholas=1). Based on observation of plumage characteristics, one territory (2.9%) was occupied by a single second-year peregrine throughout the breeding season (Santa Rosa). We found three previously active territories (8.6%) to be inactive in 2007 (San Miguel=1, Santa Rosa=1, Santa Cruz=1). Three territories (8.6%), two on Santa Catalina, which had previously been active, and one on San Nicholas, hosted winter resident peregrines that apparently migrated back to their summer territories in late February and March. We could not determine the status of one territory (West Anacapa). Access to certain areas of San Clemente Island was restricted due to active U.S. Navy training activities and our survey effort on the rest of the island was limited to one day during the annual San Clemente Loggerhead Shrike survey; therefore we were unable to confirm reports of potential peregrine falcon residency on the island. We documented 10 previously unknown or unconfirmed territories in the 2007 season.

**Figure 4. Peregrine Falcon Territories on the Northern Channel Islands.**





**Figure 5. Peregrine Falcon Territories on the Southern Channel Islands.**



\*San Clemente Island was not adequately surveyed in 2007 because of access restrictions to sensitive and active military areas.

**Table 1. Territory Status by Island.**

Islands visited	Totals	Per island							
	8	SMI	SRI	SCI	ANA	SBI	SCA	SNI	SCL
Territories visited	35	8	10	9	3	1	2	2	0
Active Territories	25	7	8	7	2	1	0	0	0
Transitional Territories	2	0	0	1	0	0	0	1	0
Occupied Territories	1	0	1	0	0	0	0	0	0
Wintering Territories	3	0	0	0	0	0	2	1	0
Inactive Territories	3	1	1	1	0	0	0	0	0
Status undetermined	1	0	0	0	1	0	0	0	0
New 2007 Territory	10	3	2	2	1	0	0	2	0
Unconfirmed Territories	3	0	0	2	0	0	0	0	1

SMI – San Miguel Island, SRI – Santa Rosa Island, SCI – Santa Cruz Island, ANA – Anacapa Islands, SBI – Santa Barbara Island, SCA – Santa Catalina Island, SNI – San Nicolas Island, SCL – San Clemente Island

## 2007 Channel Islands Peregrine Falcon Study Final Report

Each new active territory was given a nest code and added to the SCPBRG/CDFG California peregrine falcon database. We also located or received reports of three possible new peregrine territories that remain unconfirmed due to logistical difficulties or to the fact that they were discovered after the breeding season. Unconfirmed territories were not given nest codes. Table 2 shows the status, outcome, and productivity of each territory.

**Table 2. Status, Reproductive Outcome and Young Produced by Territory.**

Island	Nest Code	Territory	2007 Status	Outcome	# Chicks
SMI	MC0017	Hoffman Pt.	Active	Failed	
	MC0028	Bat Rock	Active	Failed	
	MC0057	Carbon Pt.	Active	Failed	
	MC0037	Rat Trap	Inactive		
	MC0059	Science Pt./Millennium	Active	Successful	1
	MC0047	Crooked	Active	Successful	3
	MC0044	Cardwell	Active	Failed	
	MC0058	Salvador Pt.	Active	Successful	3
SRI	MC0016	Carrington Pt.	Active	Successful	2
	MC0027a	Lime Pt. Alt. (Lobos Cyn)	Active	Successful	3
	MC0035	Jaw Gulch	Inactive		
	MC0034	Bee R. Cyn	Active	Successful	3
	MC0050	Trancion	Active	Successful	2
	MC0051	Krumholtz	Active	Successful	3
	MC0036	Lost Hat	Occupied		
	MC0031	Water Cyn.	Active	Failed	
	MC0056	Gnoma	Active	Failed	
	MC0055	Soledad	Active	Successful	2
SCI	MC0018	Gherini	Active	Failed	
	MC0045	Arch Rock	Active	Successful	2
	MC0030	Sea Lion	Active	Successful	3
	MC0020	West End	Inactive		
	MC0038	Black Pt.	Active	Failed	
	MC0019	Laguna	Active	Successful	1
	MC0046	Valley Anchorage	Active	Successful	1
	MC0053	Bowen Pt.	Active	Successful	2
	MC0052	Cavern Pt.	Transitional		
		Diablo Pt.	Unconfirmed		
ANA		Little Scorpion	Unconfirmed		
	MC0021	West Anacapa	Active	Undetermined	
	MC0043	Middle Anacapa	Undetermined		
	MC0054	East Anacapa	Active	Successful	1
SBI	MC0033	Santa Barbara	Active	Successful	3
SCA	MC0042	Long Pt.	Wintering		
	MC0049	Bullethead	Wintering		
SCL		China Pt.	Unconfirmed		
SNI		Southwest	Wintering		
		Southeast	Occ/Trans.		

## **Nest Monitoring**

We determined the breeding chronologies and/or reproductive outcomes at 24 of the 25 (95.8%) active nests on five of the eight islands.

### **Breeding Chronology**

Ten pairs laid complete clutches and began incubation by mid- to late March (Table 3). Nine pairs achieved hard incubation from the second week to the end of April. We were unable to determine a clutch completion time for one pair that was successful (Laguna). We observed no evidence of clutch completion or incubation at four territories though courtship and copulations were observed.

**Table 3. Breeding Chronologies by Territory.**

Island	Nest Code	Territory	Clutch Completion	Hatch dates	Failure dates
SMI	MC0017	Hoffman Pt.	4 <sup>th</sup> wk Mar		2 <sup>nd</sup> wk Apr
	MC0028	Bat Rock	4 <sup>th</sup> wk Mar		2 <sup>nd</sup> wk Apr
	MC0057	Carbon Pt.	4 <sup>th</sup> wk Apr		1 <sup>st</sup> wk Jun
	MC0059	Science Pt./Millennium	4 <sup>th</sup> wk Apr	5 <sup>th</sup> wk May	
	MC0047	Crooked	1 <sup>st</sup> wk Apr	2 <sup>nd</sup> wk May	
	MC0044	Cardwell	1st wk Apr/4 <sup>th</sup> wk Apr		2 <sup>nd</sup> wk Apr/4 <sup>th</sup> week May
	MC0058	Salvador Pt.	3 <sup>rd</sup> wk Mar	4 <sup>th</sup> wk Apr	
SRI	MC0016	Carrington Pt.	4 <sup>th</sup> wk Mar	2 <sup>nd</sup> wk May	
	MC0027a	Lime Pt. Alt. (Lobos)	4 <sup>th</sup> wk Apr	5 <sup>th</sup> wk May	
	MC0034	Bee Rock Cyn	1 <sup>st</sup> wk Apr	2 <sup>nd</sup> wk May	
	MC0050	Trancion	4 <sup>th</sup> wk Mar	1 <sup>st</sup> wk May	
	MC0051	Krumholtz	3 <sup>rd</sup> wk Mar	4 <sup>th</sup> wk Apr	
	MC0031	Water Cyn.	None		Undetermined
	MC0056	Gnoma	None		Undetermined
	MC0055	Soledad	2 <sup>nd</sup> wk Mar	3 <sup>rd</sup> wk Apr	
SCI	MC0018	Gherini	None		Undetermined
	MC0045	Arch Rock	1 <sup>st</sup> wk Apr	2 <sup>nd</sup> wk May	
	MC0030	Sea Lion	2 <sup>nd</sup> wk Mar	3 <sup>rd</sup> wk Apr	
	MC0038	Black Pt.	None		Undetermined
	MC0019	Laguna	Undetermined	Undetermined	
	MC0046	Valley Anchorage	4 <sup>th</sup> wk Apr	5 <sup>th</sup> wk May	
	MC0053	Bowen Pt.	2 <sup>nd</sup> wk Apr	3 <sup>rd</sup> wk May	
ANA	MC0054	East Anacapa	4 <sup>th</sup> wk Mar	1 <sup>st</sup> wk Apr	
SBI	MC0033	Santa Barbara Island.	3 <sup>rd</sup> wk Mar	3 <sup>rd</sup> wk Apr	

### **Reproductive Success/Failure**

Sixteen pairs (69.6%) successfully hatched eggs, producing 35 young, an average of 1.46 young per active nest where outcome was determined (Table 4). Eight (33.3%) nests failed to produce young either due to egg breakage during incubation (n = 2), failure to hatch eggs (n = 1), or failure to lay a full clutch of eggs this season (breaking while laying)(N = 5). We observed evidence of recycling (2<sup>nd</sup> clutch laying) after failure at SMI Cardwell which subsequently failed

## 2007 Channel Islands Peregrine Falcon Study Final Report

to hatch their 2<sup>nd</sup> clutch. We observed no evidence of 2<sup>nd</sup> clutch laying at 3 sites where complete clutches had been laid even though renewed courtship activities were observed at 3 of those sites.

**Table 4. Breeding Status and Reproductive Outcome by Island.**

BREEDING STATUS:	Totals	Per island							
		SMI	SRI	SCI	ANA	SBI	SCA	SNI	SCL
Outcome Determined	24	7	8	7	1	1			
Pairs Laid Eggs	20	7	6	5	1	1	0	0	0
Laying Undetermined*	4	0	1	2	1	0	0	0	0
Pairs hatched	16	3	6	5	1	1	0	0	0
Pairs Failed	8	4	2	2	0	0	0	0	0
Pairs Recycling	0	0	0	0	0	0	0	0	0
Number of Young	35	7	15	9	1	3	0	0	0
Young banded	26	3	15	4	1	3	0	0	0
Productivity**	1.46	1.00	2.14	1.29	1.00	3.00	0	0	0
% Failure	30.4%	57.1%	14.3%	28.6%	0.0%	0.0%	n/a	n/a	n/a

\* Never reached hard incubation

\*\* Number of young per active territory where outcome was determined.

### **Banding and Sample Collection**

Latta and Pagel banded 26 chicks at 12 nests on 5 islands (Table 5). We made 35 nest entries, collecting 39 eggshell and eggshell fragment samples representing 32 distinct clutches (eighteen 2007 clutches, fourteen 2001-2006 clutches)(Table 6). We were unsuccessful in acquiring fresh addled eggs using the Egg Buddy digital egg monitor; however, we did collect single addled eggs from SMI Carbon, SRI Bee Rock Canyon 1, SRI Bee Rock Canyon 2 and SRI Trancion during banding and sample collection climbs. Three of the addled eggs were laid in 2007, the fourth (SRI Bee Rock Canyon 2) was from an earlier clutch. We collected prey remains from 19 sites. We obtained 2 whole blood samples from resident breeding adult female peregrines from Santa Cruz and Santa Rosa Islands and identified their natal origins (Table 6). A complete list of all samples collected is presented in Appendix ii.

# 2007 Channel Islands Peregrine Falcon Study Final Report

**Table 5. Chicks Banded by Territory.**

Island	Territory	Date	Sex	USGS band number	VID
SMI	Crooked	5/27/2007	F	1807-96252	63 R
			F	1807-96253	40 Z
			M	2206-70064	85 P
SRI	Soledad	5/8/2007	F	1687-22105	05 D
			F	1687-22104	06 D
	Krumholtz	5/15/2007	F	1687-22106	13 Z
			M	1126-02007	60 D
			M	1126-02008	63 D
	Trancion	5/16/2007	F	1687-22107	43 Z
			F	1687-22108	66 Z
	Carrington Pt.	5/30/2007	F	1687-22109	21 Z
			M	1126-02010	65 D
	Bee Rock Cyn.	5/31/2007	F	1687-22110	36 Z
			F	1687-22111	23 Z
			M	1126-02011	66 D
	Lime Pt. Alt. (Lobos)	6/14/2007	F	1687-22114	89 Z
			M	1126-02012	74 D
			M	1126-02013	69 D
SCI	Sea Lion	5/11/2007	F	1807-96327	63 Z
	Bowen Pt.	6/2/2007	F	1687-22112	87 Z
			F	1687-22113	86 Z
	Valley Anchorage	6/18/2007	M	1126-02014	73 D
ANA	East Anacapa	5/17/2007	M	1126-02009	64 D
SBI	Santa Barbara Island	5/9/2007	F	1807-96326	94 Z
			M	2206-70025	85 S
			M	2206-70026	74 P

**Table 6. Samples Collected by Island.**

SAMPLES COLLECTED:	Totals		Per island							
			SMI	SRI	SCI	ANA	SBI	SCA	SNI	SCL
Nest Entries	35		13	12	6	2	2	0	0	0
Addled Eggs	4		1	3	0	0	0	0	0	0
Eggshells & Fragments	39		15	14	6	1	3	0	0	0
Clutch samples	32		14	10	6	1	1	0	0	0
Blood for contaminants	2		0	1	1	0	0	0	0	0
Prey Remains Samples	17		3	6	6	1	1	0	0	0

**Table 7. Breeding Territory and Natal Origin of Two Resident Adult Females.**

Band Number	Breeding Territory	Hatch Year	Natal Origin	Fledged From
1807-28200	SCI Sea Lion	1995	Wild island nest	SRI Water Cyn
1807-96222	SRI Lime Pt. Alt. (Lobos Cyn)	2004	Captive bred	Sanford Winery Hacksite*

\*Santa Ynez Valley, CA

## Sample Analysis

### **Eggshell Measurements**

Average eggshell thickness, and its correlate term “percent thinning”, is a numerical way to represent the clutch mean of fragment samples of eggs or a grouping of fragments (Ratcliffe 1970). Table 8 shows the clutch means of eggshell thickness and percent thinning for all 18 of the eyries sampled in 2007 as well as the averages of clutch means by island. The average of the clutch means for all of the 2007 samples was 0.297 mm or 18.34 % thin. Individual clutch means ranged from 8.9% thin at SRI Trancion to 28.72% thin at SMI Science/Millennium. Clutch means averaged by island ranged from 12.69% thin on Santa Rosa Island to 23.30% thin on Santa Barbara Island.

**Table 8. Eggshell Measurements of 2007 Samples**

Island	Territory	Clutch Means			Island Means	
		Thickness (mm)	% Thin		Thickness (mm)	% Thin
SMI	Hoffman Pt.	0.312	14.34		0.291	20.16
	Bat Rock	0.287	21.11			
	Cardwell Pt.	0.313	13.94			
	Carbon	0.273	24.91			
	Crooked	0.317	12.79			
	Salvador	0.289	20.49			
	Science/Millennium	0.259	28.72			
SRI	Carrington	0.322	11.66		0.318	12.69
	Lime Pt. Alt. (Lobos)	0.301	17.40			
	Bee Rock Cyn.	0.324	10.93			
	Krumholtz	0.299	17.86			
	Trancion	0.335	8.09			
	Soledad	0.304	16.50			
SCI	Sea Lion	0.302	16.94		0.285	21.70
	Bowen Pt.	0.282	22.46			
	Valley Anchorage	0.267	26.71			
ANA	East Anacapa	0.297	18.43		0.297	18.43
SBI	Santa Barbara Island	0.279	23.30		0.279	23.30
<b>Total average</b>		<b>0.297</b>	<b>18.34</b>			

Table 9 shows the clutch means and island means from all pre-2007 (1988-2006) samples (N = 70) collected either during this study or opportunistically during prior visits (1995-2006), as well as those collected during Hunt's 1994 study (1992-1994) and SCPBRG's peregrine falcon recovery efforts (1989-1990). The clutch means of these samples averaged 17.87% thin. The individual clutch means in these samples ranged from -1.27% thin for SMI Cardwell Point, laid sometime between 2002-2005 and 33.24% thin for SRI Carrington 2003 2<sup>nd</sup> clutch, though this latter sample only consisted of one fragment. The sample with the next highest thinning was from SMI Cardwell Point in 2003 and averaged 29.18 % thin. Clutch means averaged by island

# 2007 Channel Islands Peregrine Falcon Study Final Report

were 19.41%, 14.5%, 19.52%, 18.73%, and 21.70% thin for SMI, SRI, SCI, ANA, and SBI respectively.

**Table 9. Eggshell Measurements of 1988-2006 Channel Islands Samples.**

Island	Territory	Approximate Year Laid	Clutch Means			Island Means	
			Thickness (mm)	% Thin		Thickness (mm)	% Thin
SMI	Hoffman Pt.	2006	0.279	23.22		0.293	19.41
	Hoffman Pt.	<2006	0.288	20.96			
	Hoffman Pt.	<2006	0.303	16.76			
	Hoffman Pt.	<2006	0.288	20.77			
	Hoffman Pt.	1993	0.288	20.77			
	Hoffman Pt.	1992	0.280	23.02			
	Hoffman Pt.	1990	0.278	23.54			
	Hoffman Pt.	1989	0.289	20.61			
	Hoffman Pt.	1988	0.302	17.03			
	Bat Rock	<2007	0.306	15.98			
	Bat Rock	1998	0.301	17.31			
	Bat Rock	1994	0.308	15.38			
	Bat Rock	1993	0.289	20.60			
	Bat Rock	1992	0.295	19.01			
	Rat Trap	1999	0.279	23.30			
	Cardwell Pt.	<2007	0.369	-1.27			
	Cardwell Pt.	2003	0.258	29.18			
SRI	Carrington	2006	0.300	17.68		0.311	14.50
	Carrington	2003 1 <sup>st</sup> clutch	0.308	15.17			
	Carrington	2003 2 <sup>nd</sup> clutch*	0.243	33.24			
	Carrington	1995	0.294	19.23			
	Lime Pt.	1992	0.298	18.04			
	Lime Pt. Alternate	1997	0.347	4.70			
	Lime Pt. Alternate	1998 1 <sup>st</sup> clutch	0.323	11.26			
	Lime Pt. Alternate	1998 2 <sup>nd</sup> clutch	0.301	17.31			
	Water Canyon	2006	0.317	12.95			
	Water Canyon	2003	0.292	19.75			
	Water Canyon	>2000	0.334	8.15			
	Water Canyon	1998	0.326	10.44			
	Water Canyon	1995	0.307	15.66			
	Bee Rock Cyn.	<2007	0.336	7.2			
	Bee Rock Cyn.	1998	0.301	17.31			
	Bee Rock Cyn.	1997	0.354	2.75			
	Lost Hat	1998	0.328	9.89			
SCI	West End	2003	0.294	19.37		0.293	19.52
	West End	1993	0.312	14.29			
	West End	1992 1 <sup>st</sup> clutch	0.280	23.09			
	West End	1992 2 <sup>nd</sup> clutch	0.292	19.80			
	West End	1989	0.270	25.82			
	Gherini	<2007	0.332	8.9			

## 2007 Channel Islands Peregrine Falcon Study Final Report

	Gherini	1994	0.280	23.08		
	Gherini	1992	0.288	20.76		
	Laguna	1992	0.290	20.33		
	Sea Lion	1993	0.288	20.88		
	Black Pt.	2003	0.287	21.2		
	Black Pt.	2002	0.299	17.7		
	Black Pt.	2001	0.301	17.2		
ANA	West Anacapa	1998	0.269	26.10	0.296	18.73
	West Anacapa	1994	0.305	16.21		
	West Anacapa	1993	0.305	16.21		
	West Anacapa	1992	0.294	19.03		
	West Anacapa	1989	0.308	15.38		
SBI	Santa Barbara Is.	1997	0.285	21.70	0.285	21.70
<b>Average</b>			<b>0.299</b>	<b>17.87</b>		

\* Sample consists of one fragment only.

Appendix v contains a table of measurements of all individual eggs, eggshells, and fragments collected from the Channel Islands from 1999 to 2007 and used to determine the clutch means reported in the Results section.

### Contaminant Analysis

Latta and Pagel collected 4 addled eggs from 4 different eyries at 3 territories on 2 islands. Data on whole egg volume and weight were not available to adjust concentrations for the loss of water and lipid that occurs between when an egg is freshly laid and when it is collected. The percent solids was essentially the same for all four eggs (range 18%-22%). Consequently, while it was not possible to estimate the fresh weight-based concentrations of contaminants, it can still be noted that differences between wet weight-based contaminant levels in eggs would not be due to differences in the conditions of the eggs.

Reported detection limits for DDTs and metabolites ranged from 0.15 µg/kg wet weight (ww) to 16 µg/kg, depending on the need for dilution due to high concentrations of target analyte. The reported detection limits for PCB congeners ranged from 0.05 µg/kg ww to 6 µg/kg depending on dilution factors and detection limits for PCB homolog classes were all approximately 0.3 µg/kg.

The levels of DDT isomers (4, 4'-DDE, 4, 4'-DDD, and 4, 4'-DDT) and PCB congeners are presented in Table 10. Concentrations are reported in micrograms per kilogram (µg/kg or parts per billion) of wet weight. DDT concentrations are also shown in parts per million (ppm) in this text for comparison with other studies. The geometric mean DDE level for all four samples was 9597 µg/kg (9.6 ppm). The range was 2650 to 57,900 µg/kg (2.7 to 57.9 ppm). Forty PCB congeners were detected. The geometric mean of the sums of those congeners for each egg was 2058 µg/kg (2.1 ppm) and the range was 460 to 14,347 µg/kg (0.5 to 14.3 ppm). Whole blood samples collected from two adult peregrine falcons were not analyzed.



# 2007 Channel Islands Peregrine Falcon Study Final Report

**Table 10. Levels of DDTs and PCBs in four peregrine falcon eggs collected in 2007.**

Eyrie: Sample:	SMI Carbon Pt. MC-57	SRI Bee Rock Cyn 1 MC-34-1	SRI Bee Rock Cyn 2 MC-34-2	SRI Trancion MC-50	Mean
Percent Lipid	5.67	4.67	5.52	3.95	4.90
4,4' -DDE	57900	4220	2650	13100	9596.81
4,4' -DDT	7.32	0.78	3.86	3.16	2.89
4,4' -DDD	1.4	0.82	3.12	0.36	1.07
Total DDTs	57908	4222	2157	13104	9117.54
PCBs*					
28	11.3	1.73	1.52	2.84	3.03
37	0.23	U	U	U	0.23
43	0.17	U	0.195	U	0.18
52	0.133	U	0.331	U	0.21
66	65.2	5	4.14	12.2	11
70	1.48	0.268	0.686	0.37	0.56
74	68.8	5.46	4.99	18.9	14
87	22.9	1.17	1.22	4.69	3.52
101, 84	14.2	0.723	2.36	1.69	2.53
99	672	22	17.9	128	76
105	184	12.1	8.82	46	31
110	0.994	U	0.112	0.164	0.26
114	11.6	0.997	0.822	4.63	2.58
118	1140	58.7	42	307	171
119	6.47	0.225	0.166	0.618	0.62
123	8.95	0.851	0.633	2.85	1.93
132, 168	4.31	U	0.225	1.39	1.10
138, 163	2250	84.8	63.1	704	303
149	17.9	1.36	0.805	4.03	2.98
151	0.152	U	0.124	U	0.14
153	4470	175	114	1310	585
156	91	8.92	6.69	37.9	21
157	18.3	1.45	1.08	6.64	3.71
158	66	2.62	1.99	18.4	8.92
167, 128	268	17	12.7	97.7	49
170, 190	403	27.8	19.1	142	74
177	93	4.1	3.29	28.8	14
180	2270	78	51.2	656	278
182, 187	834	31.5	24	231	110
183	478	16.9	11.8	125	59
189	11.8	1.49	1.19	5.05	3.21
194	231	22.6	15.3	84.2	51
195	54.3	4.57	3.17	18.5	11
196, 203	264	21.4	15.1	98.3	54
201	222	16	13.2	90	45
206	69	13.3	11.3	26.8	23
209	18.1	4.66	3.68	8.04	7.07
Non-ortho-PCBs					
77	4.66	0.353	0.846	1.37	1.18
126	U	U	0.319	U	0.32
169	0.454	U	U	0.242	0.33
Sum of congeners	14342	643	459	4224	2056

\* IUPAC numbers according to Ballschmitter and Zell (1980)

U = undetected

### Prey Remains

Latta and Pagel collected prey remains from 19 different eyries on 5 islands. N. John Schmitt keyed out a total of 182 individual prey items representing 49 species (Table 11). Eighteen prey items could only be keyed out to genus and 9 were identified as “unknown passerine”. For the purposes of the report we assigned habitat types of Sea, Land, or Shore to prey species, according to whether they forage primarily in aquatic, terrestrial, or shoreline habitats, in order to compare the potential pathways of bioaccumulative contaminants with the analyses of reproductive outcome, eggshell thinning, and contaminant levels in Channel Islands peregrine falcons in 2007. Sea birds represented 69% of the biomass and 40% of the mean number of individuals (MNI) (Figures 6 and 7). Land birds represented 23% and 56% and shorebirds 8% and 5% of the biomass and MNI respectively. When calculated using percent of total biomass as the metric (Table 12), the most predominant prey species were western gull (18%), pigeon guillemot (14%), Cassin’s auklet (7%), and Xantus’ murrelet (5%). The predominant species in terms of MNI from the combined samples was red phalarope (n=20), followed by black-headed grosbeak (n=12), Cassin’s auklet (n=10), unknown passerine (n=9), red-necked phalarope (n=8), western tanager (n=8), and western meadowlark (n=7). Table 13 shows the MNI, total biomass, and percent biomass of the combined prey sample by habitat type.

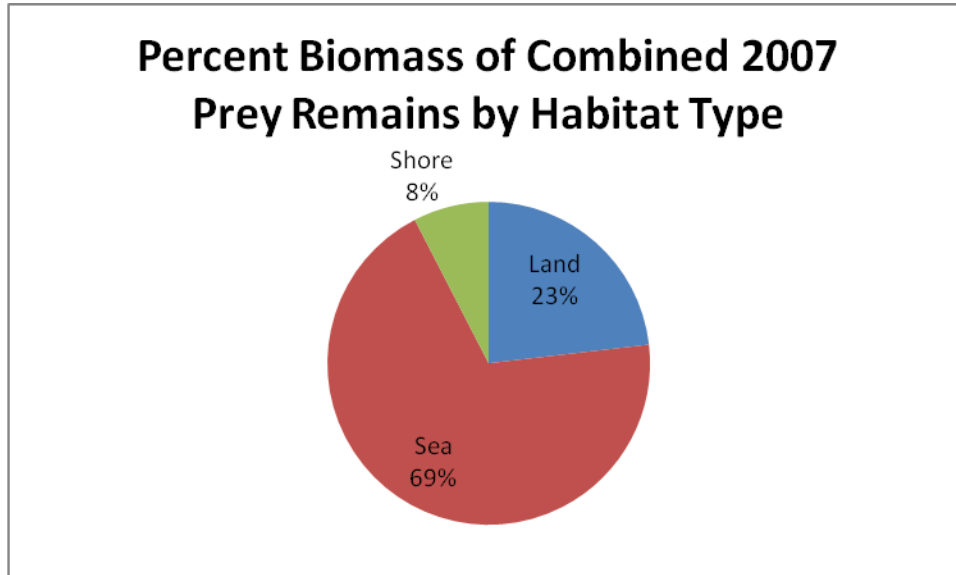
**Table 11. 2007 Prey Items Collected (MNI) by Island.**

Family	Genus species	Common name	SMI	SRI	SCI	ANA	SBI	Totals
Ducks	<i>Anas platyrhynchos</i>	Mallard		1				1
Grebes	<i>Podiceps?</i>	Grebe sp.	1		1			2
	<i>Podiceps nigricollis</i>	Eared grebe	1					1
	<i>Podiceps auritus</i>	Horned grebe			1			1
	<i>Aechmophorous sp.</i>	Western/Clark’s Grebe			1			1
Storm Petrels	<i>Oceanodroma sp.</i>	Storm petrel sp.	1		2			3
Falcons	<i>Falco sparverius</i>	American kestrel			2			2
Sandpipers	<i>Numenius phaeopus</i>	Whimbrel			1	1	1	3
	<i>Numenius americanus</i>	Long-billed curlew	1					1
	<i>Calidris alba</i>	Sanderling	1					1
	<i>Calidris mauri</i>	Western sandpiper	1					1
	<i>Limnodromus</i>	Dowitcher sp.	1	1	1			3
Phalaropes	<i>Phalaropus</i>	Phalarope sp.	1					1
	<i>Phalaropus lobatus</i>	Red-necked phalarope	2		5		1	8
	<i>Phalaropus fulicaria</i>	Red phalarope	7	7	4	1	1	20
Gulls	<i>Larus canus</i>	Mew gull	1					1
	<i>Larus occidentalis</i>	Western gull		1	2	1	1	5
	<i>Larus californicus</i>	California gull			1			1
Terns	<i>Sterninae</i>	Tern sp		2				2
	<i>Chlidonias niger</i>	Black tern	1	1	1			3
Alcids	<i>Cephus columba</i>	Pigeon guillemot	1	5	2			8
	<i>Synthliboramphus hypoleucus</i>	Xantus' murrelet	1	1	1		1	4
	<i>Ptychoramphus aleuticus</i>	Cassin's auklet	5	5				10
Doves	<i>Streptopelia decaocto</i>	Eurasian collared dove	1				1	2
	<i>Zenaida macroura</i>	Mourning dove			3		2	5
Goatsuckers	<i>Chordeiles acutipennis</i>	Lesser nighthawk			1			1

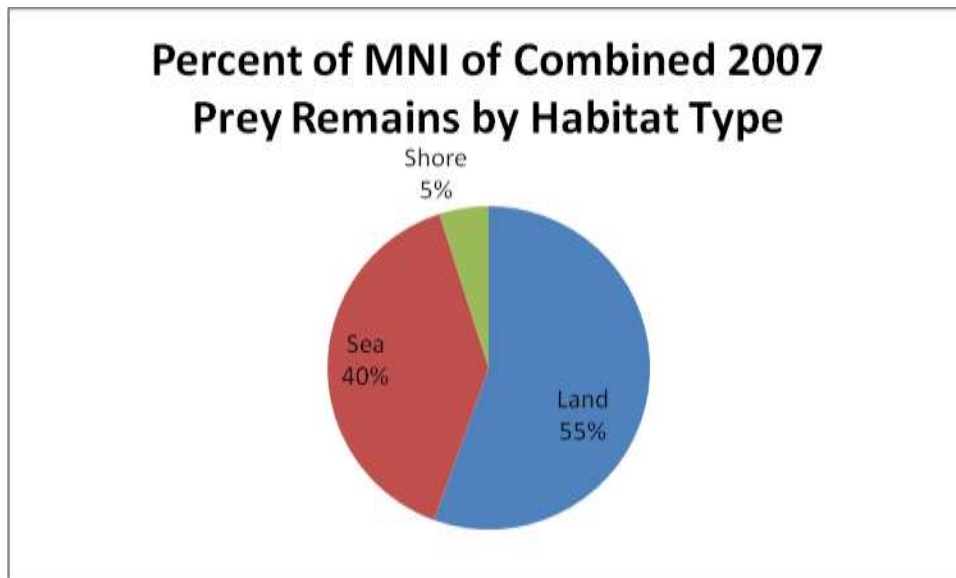
## 2007 Channel Islands Peregrine Falcon Study Final Report

Hummingbirds	<i>Archilochus alexandri</i>	Black-chinned hummingbird					1	1
Woodpeckers	<i>Colaptes auratus</i>	Northern flicker	1					1
Unk. Passerine			3	3	3			9
Tyrant Flycatchers	<i>Tyrannus verticalis</i>	Western kingbird					1	1
	<i>Myiarchus cinerascens</i>	Ash-throated flycatcher			1		1	2
	<i>Sayornis nigricans</i>	Black phoebe		1				1
Empidonax Flycatchers	<i>Empidonax</i>	Flycatcher sp.		1				1
	<i>Empidonax difficilis</i>	Pacific slope flycatcher					1	1
Corvids	<i>Aphelocoma insularis</i>	Island scrub-jay			1			1
	<i>Corvus corax</i>	Common raven			1			1
Nuthatches	<i>Sitta canadensis</i>	Red-breasted nuthatch					1	1
Wrens	<i>Troglodytes aedon</i>	House wren					1	1
	<i>Salpinctes obsoletus</i>	Rock wren	1					1
Thrushes	<i>Catharus guttatus</i>	Hermit thrush			1		4	5
	<i>Ixoreus naevius</i>	Varied thrush					1	1
Starlings	<i>Sturnus vulgaris</i>	European starling		1				1
Warblers	<i>Vermivora celata</i>	Orange-crowned warbler		1		1	2	4
	<i>Dendroica</i>	Hermit/Townsend's/Black-throated gray					1	1
	<i>Dendroica coronata</i>	Yellow-rumped warbler					1	1
	<i>Dendroica petechia</i>	Yellow warbler		1				1
	<i>Wilsonia</i>	Likely Wilson's	1				3	4
	<i>Wilsonia pusilla</i>	Wilson's warbler			1			1
Sparrows	<i>Melospiza melodia</i>	Song sparrow	1	1	1			3
	<i>Zonotrichia leucophrys</i>	White-crowned sparrow			1		3	4
	<i>Passerella lilaca</i>	Fox sparrow	1		1			2
Tanagers	<i>Piranga ludoviciana</i>	Western tanager	2			1	5	8
Grosbeaks	<i>Pheucticus melanocephalus</i>	Black-headed grosbeak	1	2	2		7	12
Buntings	<i>Passerina amoena</i>	Lazuli bunting					1	1
Blackbirds/orioles	<i>Sturnella neglecta</i>	Western meadowlark		6	1		1	8
	<i>Euphagus cyanocephalus</i>	Brewer's blackbird		1				1
	<i>Icterus bullockii</i>	Bullock's oriole	1				1	2
	<i>Icterus cucullatus</i>	Hooded oriole		1			1	2
Finches	<i>Carpodacus mexicanus</i>	House finch	1	3	3			7
<b>Totals</b>			<b>40</b>	<b>46</b>	<b>46</b>	<b>5</b>	<b>45</b>	<b>182</b>

**Figure 6. Percent Biomass by Habitat Type of Prey Remains collected on all Channel Islands combined in 2007.**



**Figure 7. Percent MNI by Habitat Type of Prey Remains collected on all Channel Islands combined in 2007.**



# 2007 Channel Islands Peregrine Falcon Study Final Report

**Table 12. MNI, Total and Percent Biomass of 2007 Prey Items by Species.**

Genus species	Common name	Type	No.	Mean Mass (g)	Total Biomass	Percent Biomass
<i>Anas platyrhynchos</i>	Mallard	sea	1	1082	1082	3.85%
<i>Podiceps?</i>	Grebe sp.	sea	2	372.5	745	2.65%
<i>Podiceps nigricollis</i>	eared grebe	sea	1	339.8	339.8	1.21%
<i>Podiceps auritus</i>	Horned Grebe	sea	1	453	453	1.61%
<i>Aechmophorous sp.</i>	Western/Clark's Grebe	sea	1	1200	1200	4.27%
<i>Oceanodroma</i>	Storm Petrel sp.	sea	3	43.6	130.8	0.47%
<i>Falco sparverius</i>	American kestrel	land	2	115.5	231	0.82%
<i>Numenius phaeopus</i>	Whimbrel	shore	3	379.5	1138.5	4.05%
<i>Numenius americanus</i>	Long-billed curlew	shore	1	586.5	586.5	2.09%
<i>Calidris alba</i>	Sanderling	shore	1	59.8	59.8	0.21%
<i>Calidris mauri</i>	western sandpiper	shore	1	25.6	25.6	0.09%
<i>Limnodromus</i>	Dowitcher sp.	shore	3	106.5	319.5	1.14%
<i>Phalaropus</i>	Phalarope sp.	sea	1	44.7	44.7	0.16%
<i>Phalaropus lobatus</i>	Red-necked phalarope	sea	8	33.8	270.4	0.96%
<i>Phalaropus fulicaria</i>	Red phalarope	sea	20	55.7	1114	3.97%
<i>Larus canus</i>	mew gull	sea	1	388.5	388.5	1.38%
<i>Larus occidentalis</i>	Western gull	sea	5	1011	5055	18.00%
<i>Larus californicus</i>	California gull	sea	1	670.34	670.34	2.39%
<i>Sterninae</i>	Tern sp	sea	2	246	492	1.75%
<i>Chlidonias niger</i>	Black tern	sea	3	65.3	195.9	0.70%
<i>Cepphus Columba</i>	Pigeon guillemot	sea	8	487	3896	13.87%
<i>Synthliboramphus hypoleucus</i>	Xantus' murrelet	sea	4	375	1500	5.34%
<i>Ptychoramphus aleuticus</i>	Cassin's auklet	sea	10	188	1880	6.69%
<i>Streptopelia decaocto</i>	Eurasian collared dove	land	2	149	298	1.06%
<i>Zenaida macroura</i>	Mourning dove	land	5	119	595	2.12%
<i>Chordeiles acutipennis</i>	Lesser nighthawk	land	1	49.9	49.9	0.18%
<i>Archilochus alexandri</i>	Black-chinned hummingbird	land	1	3.4	3.4	0.01%
<i>Colaptes auratus</i>	Northern flicker	land	1	126.5	126.5	0.45%
	Unk. passerine	land	9	127.2	1144.8	4.08%
<i>Tyrannus verticalis</i>	Western kingbird	land	1	39.6	39.6	0.14%
<i>Myiarchus cinerascens</i>	Ash-throated flycatcher	land	2	27.2	54.4	0.19%
<i>Sayornis nigricans</i>	Black phoebe	land	1	18.7	18.7	0.07%
<i>Empidonax</i>	Flycatcher sp.	land	1	11.1	11.1	0.04%
<i>Empidonax difficilis</i>	Pacific slope flycatcher	land	1	10	10	0.04%
<i>Aphelocoma insularis</i>	Island scrub-jay	land	1	120.5	120.5	0.43%
<i>Corvus corax</i>	Common raven	land	1	1225	1225	4.36%
<i>Sitta Canadensis</i>	Red-breasted nuthatch	land	1	9.8	9.8	0.03%
<i>Troglodytes aedon</i>	House wren	land	1	10.9	10.9	0.04%
<i>Salpinctes obsoletus</i>	Rock wren	land	1	16.5	16.5	0.06%
<i>Catharus guttatus</i>	Hermit thrush	land	5	31	155	0.55%
<i>Ixoreus naevius</i>	Varied thrush	land	1	77.7	77.7	0.28%
<i>Sturnus vulgaris</i>	European starling	land	1	82.3	82.3	0.29%
<i>Vermivora celata</i>	Orange-crowned warbler	land	4	9	36	0.13%
<i>Dendroica</i>	Warbler sp.	land	1	7.7	7.7	0.03%
<i>Dendroica coronata</i>	Yellow-rumped warbler	land	1	12.1	12.1	0.04%

## 2007 Channel Islands Peregrine Falcon Study Final Report

<i>Dendroica petechia</i>	Yellow warbler	land	1	9.5	9.5	0.03%
<i>Wilsonia</i>	Warbler sp.	land	4	8.8	35.2	0.13%
<i>Wilsonia pusilla</i>	Wilson's warbler	land	1	7.7	7.7	0.03%
<i>Melospiza melodia</i>	Song sparrow	land	3	19.4	58.2	0.21%
<i>Zonotrichia leucophrys</i>	White-crowned sparrow	land	4	27.6	110.4	0.39%
<i>Passerella iliaca</i>	Fox sparrow	land	2	32.3	64.6	0.23%
<i>Piranga ludoviciana</i>	Western tanager	land	8	28.1	224.8	0.80%
<i>Pheucticus melanocephalus</i>	Black-headed grosbeak	land	12	42	504	1.79%
<i>Passerina amoena</i>	Lazuli bunting	land	1	15.5	15.5	0.06%
<i>Sturnella neglecta</i>	Western meadowlark	land	8	100.7	805.6	2.87%
<i>Euphagus cyanocephalus</i>	Brewer's blackbird	land	1	62.7	62.7	0.22%
<i>Icterus bullockii</i>	Bullock's oriole	land	2	33.6	67.2	0.24%
<i>Icterus cucullatus</i>	Hooded oriole	land	2	24.3	48.6	0.17%
<i>Carpodacus mexicanus</i>	House finch	land	7	21.4	149.8	0.53%
<b>Totals</b>			<b>182</b>	<b>28087.04</b>	<b>100.00%</b>	

\* Species/sub sp. used to calculate average mass.

**Table 13. MNI, Total Biomass, and Percent Biomass of Prey Items by Habitat Type for Islands Combined.**

Type	Seabirds	Shorebirds	Land birds
MNI	72	9	101
Total Biomass	19457.4	2129.9	6499.7
Percent Biomass	69.28%	7.80%	23.14%

## DISCUSSION

From complete extirpation as a breeding species (Kiff 1980) by the 1950s, the Channel Islands subpopulation of peregrine falcons has become re-established to the northern islands through releases of captive-bred young, natural recruitment from the re-established mainland eyries and more recently from inter-island recruitment from successful pairs (See Table 14). The islands subpopulation is nearing 30 pairs, which Hunt (1994) predicted could be supported by the archipelago based on the information at that time. Our 2007 survey and monitoring effort revealed 25 active pairs on 5 of the eight islands. The fact that the three southern Channel Islands are similar in size and habitat suitability to the three largest northern islands suggest the possibility that, even though they have yet to be re-colonized to a similar extent, they may be able to support similar numbers of breeding pairs. Therefore, the true carrying capacity of the entire Channel Islands archipelago may be higher than previously predicted.

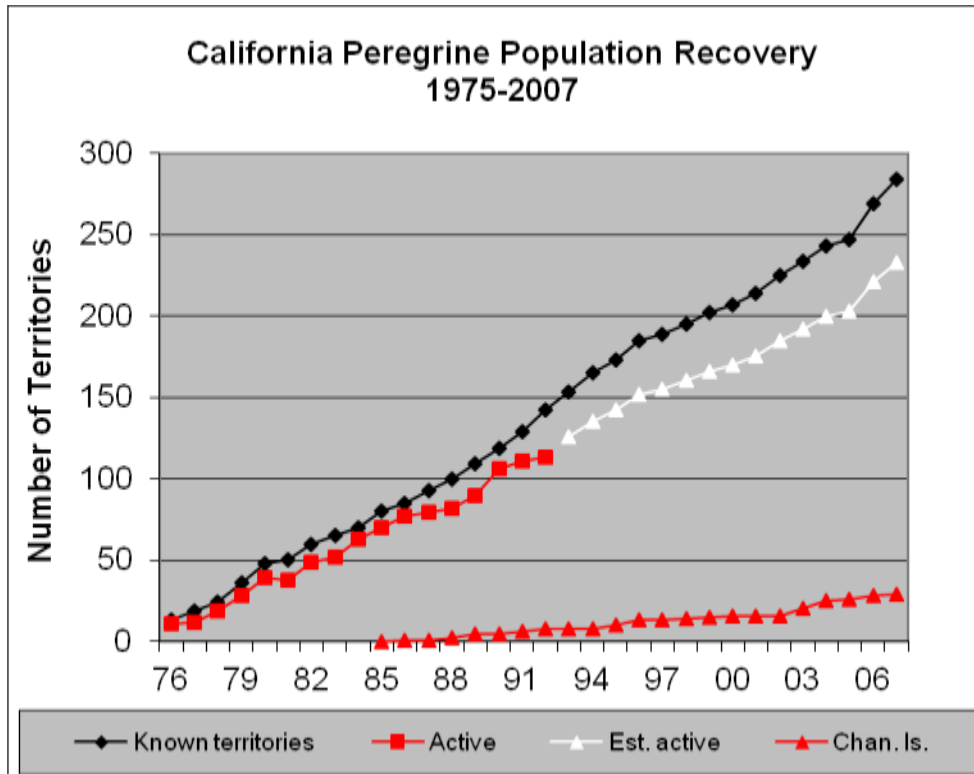
## Surveys

The Channel Islands present logistical difficulties for peregrine falcon breeding surveys. The peregrine breeding season runs from January to July. Surveys are most effectively conducted early in the breeding season, prior to egg laying, a period which, unfortunately, coincides with the worst weather conditions on the islands. 2007 was no exception. Bad weather, limited logistical access, and the presence of breeding endangered California brown pelicans (*Pelecanus*

*occidentalis*) prevented a thorough survey of Middle and West Anacapa Islands, each of which have been known to support active peregrine pairs in recent years. Restricted access due to ongoing hazardous military activities prevented thorough surveys of San Clemente Island. A report of a pair of peregrine falcons near China Point on that island remains unsubstantiated (Author's note: In 2011 an active peregrine nest site was confirmed on San Clemente Island).

Re-establishment of breeding pairs to the Channel Islands has continued apace with the recovery of the greater California subpopulation (Fig. 8). However, the recovery is much more robust in the northern islands while the southern islands lag far behind. With only four unconfirmed territories, Santa Catalina, San Clemente, and San Nicholas Islands have yet to be re-colonized to the extent of their northern counterparts. Reasons for this lag in re-colonization remain unclear. The southern islands do not support the number and diversity of resident prey species of the northern islands. Military activities and civilian development of the southern islands may have degraded the available breeding and foraging habitat. Another hypothesis is that due to the proximity of the southern islands to the sub-marine DDT dumpsite, peregrine falcons dispersing to the those islands may become too contaminated with DDE to breed successfully. However, one would expect a pair to become established, hold a territory, and produce thin-shelled eggs for a number of years if this was the case. In any case, a more thorough survey and monitoring effort of the southern islands are warranted.

**Figure 8. California vs. Channel Islands Peregrine Population Recovery.**



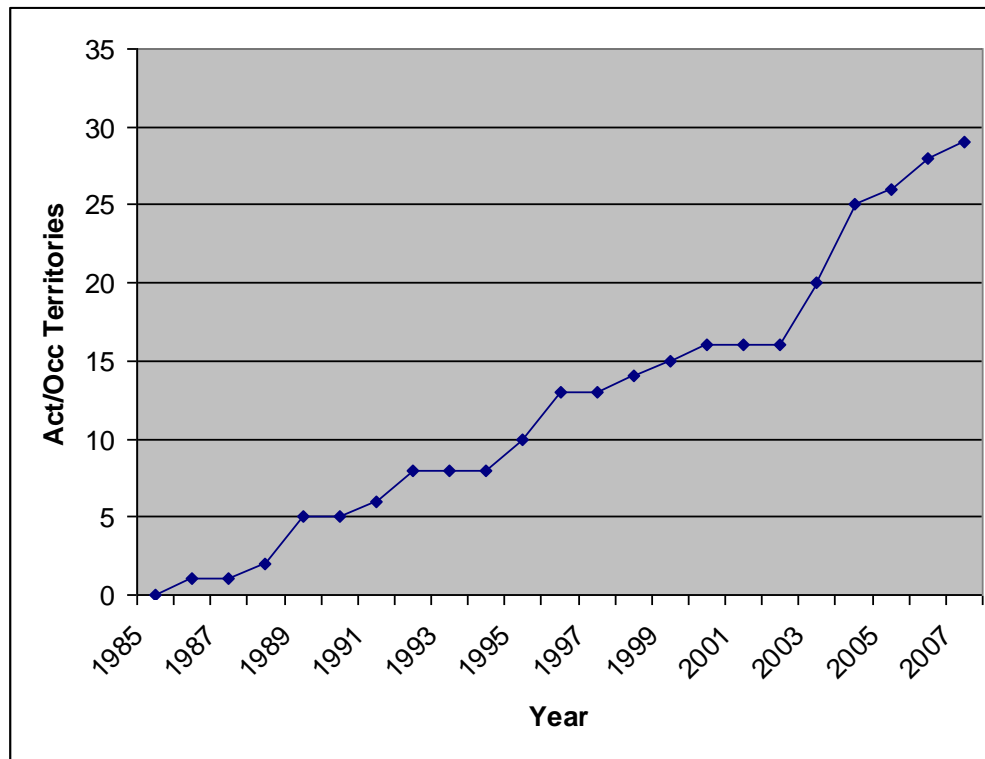
That said, the one bright spot in the recovery of the southern Channel Islands is the successful breeding on Santa Barbara Island in 2007 since the population decline in the 1950s (Figure 9). Peregrines were first documented returning to the island in 1992 and, since their first documented breeding attempt in 1996, have failed every year until 2007, when they produced three chicks. This is despite having 23.3% eggshell thinning (clutch mean).

Appendix iii shows the chronology of the Channel Islands' peregrine recovery by island as estimated using the best available evidence from SCPBRG surveys, nest manipulations, and non-SCPBRG observer accounts. The current number of active and occupied territories (Fig. 10) on the islands exceeds Kiff's (2000) historical estimate of 15-16 pairs and approaches the carrying capacity of at least 30 pairs predicted by Hunt (1994).

**Figure 9. Newly hatched Peregrine Falcon Nestlings and unhatched egg in 2007 Santa Barbara Island Eyrie. (photo B. Latta)**





**Figure 10. Channel Islands Peregrine Population Recovery.****Monitoring**

Breeding chronologies appeared to be atypical in the 2007 breeding season. Nine of the territories that laid complete clutches this season averaged 2.86 weeks late (range 0-6) when compared to records of previous seasons' laying dates (SCPBRG unpublished data). No recycling attempts were detected so we assume these were first clutches. Due to the fact that the delay in laying was spread fairly evenly across the islands we assume that heavy spring storms may have been the cause.

Initial recruitment of peregrines to the island breeding subpopulation was primarily from the dispersing birds of mainland natal origin (Hunt 1994). As island pairs began to reproduce, recruitment from inter-island dispersers supplemented the mainland recruitment (SCPBRG band return records). Of the 17 breeding peregrine falcons captured on the islands between 1992 and 2007, eight are known to have mainland natal origins, three fledged from island nests, one fledged from the San Miguel Island hack site, and five were unbanded and their natal origin is unknown (Table 14).

**Table 14. Natal Origin of Adult Breeding Peregrine Falcons Captured on the Channel Islands from 1992 - 2007.**

<b>Breeding Territory</b>	<b>Origin</b>	<b>Sex</b>	<b>Date Captured</b>	<b>Band Number</b>	<b>Trapper(s)</b>	<b>Natal Location/Year</b>
SCI Sea Lion	Island	Female	5/23/2007	1807-28200	B. Latta	SRI Water Cyn, 1995
SMI Bat Rock	Island	Male	5/29/1995	816-64353	B. Latta, A. Lewis	San Miguel Is. Hack Site, 1985
SRI Water Canyon	Island	Male	5/3/1995	1807-28286	B. Latta, M. Siemens	SCI West End, 1992
SRI Water Canyon	Island	Female	5/3/1995	1807-28285	B. Latta, M. Siemens	Anacapa Is., 1992
Anacapa	Mainland	Female	3/19/1992	987-77292	S. Francis, W. Hunt, L. Aulman	Avila Beach, 1986
SCI Gherini	Mainland	Female	3/8/1992	987-77248	S. Francis, B. Latta, W. Hunt, L. Aulman	Diablo Cyn, 1985
SCI Laguna Canyon	Mainland	Female	6/4/1995	987-77396	B. Latta, A. Lewis	Union Bank, 1989
SCI West End	Mainland	Female	3/29/1992	987-77015	S. Francis, W. Hunt, L. Aulman	Diablo Cyn, 1987
SMI Bat Rock	Mainland	Female	4/20/1992	987-93944	S. Francis, B. Latta	Banded as an immature, Marin Headlands, 1989
SMI Hoffman Pt.	Mainland	Female	1/13/1993	1807-28124	S. Francis, R. Laird, T. Swem, B. Latta, M. Robertson	Mainland, unbanded, first observed Hoffman Pt. in 1986
SRI Lime Point	Mainland	Female	1/23/1993	1807-03374	S. Francis, R. Laird	Hacked Muir Beach, 1990
SRI Lime Pt. Alt. (Lobos)	Mainland	Female	6/13/2007	1807-96222	B. Latta, J. Pagel	Sanford Winery Hacksite, 2004
SMI Hoffman Pt	Unk	Male	5/30/1995	2206-13230	B. Latta, A. Lewis	Unknown
SRI Carrington Point	Unk	Female	5/4/1995	1807-28199	B. Latta, M. Siemens	Unknown
SRI Lime Point	Unk	Male	1/22/1993	2206-13187	B. Latta, J. Gilardi	Unknown
SRI Lost Hat	Unk	Female	6/11/1998	1807-70111	B. Latta	Unknown
SRI Lost Hat	Unk	Male	6/11/1998	2206-48047	B. Latta	Unknown

Both sources continue to be in play today as evidenced by the identification of two breeding females captured by Latta and Pagel in 2007. One female on Santa Cruz Island fledged from a Santa Rosa Island nest in 1995 and a female on Santa Rosa Island fledged from a mainland hack site in 2004.

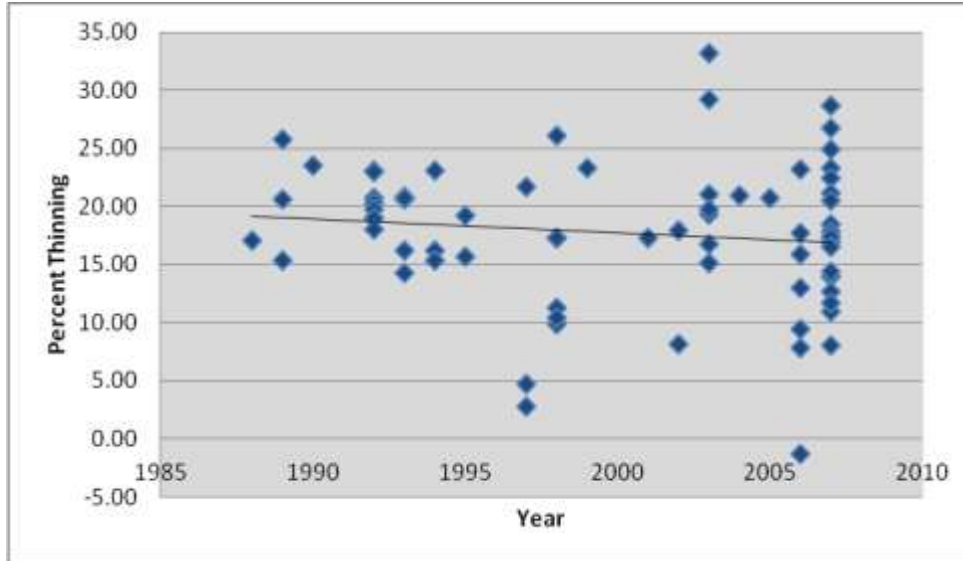
### **Reproductive Success and Eggshell Thinning**

The correlation between peregrine falcon reproductive success and DDT-induced eggshell thinning has been well documented. It is widely accepted that a population-wide average eggshell thinning of 17% or greater reduces productivity to the point of population decline (Peakall and Kiff 1988, Peakall et al. 1990, Blus 2011). It is important to note that this 17% threshold is applied to a “population” and that, due to the degree of recruitment from and emigration to the mainland, peregrines breeding on the Channel Islands cannot be considered a population separate from the mainland.

Mean eggshell thinning for the islands combined in 2007 (18.34%) is lower than the 19.4% reported by Hunt (1994) for 1992-93 but higher than the combined average of clutch means of 17.87% for all clutch samples collected from the Channel Islands since recovery began in 1987

up until this study ( $n = 53$ ). Figure 11 shows a decreasing trend in eggshell thinning over that period.

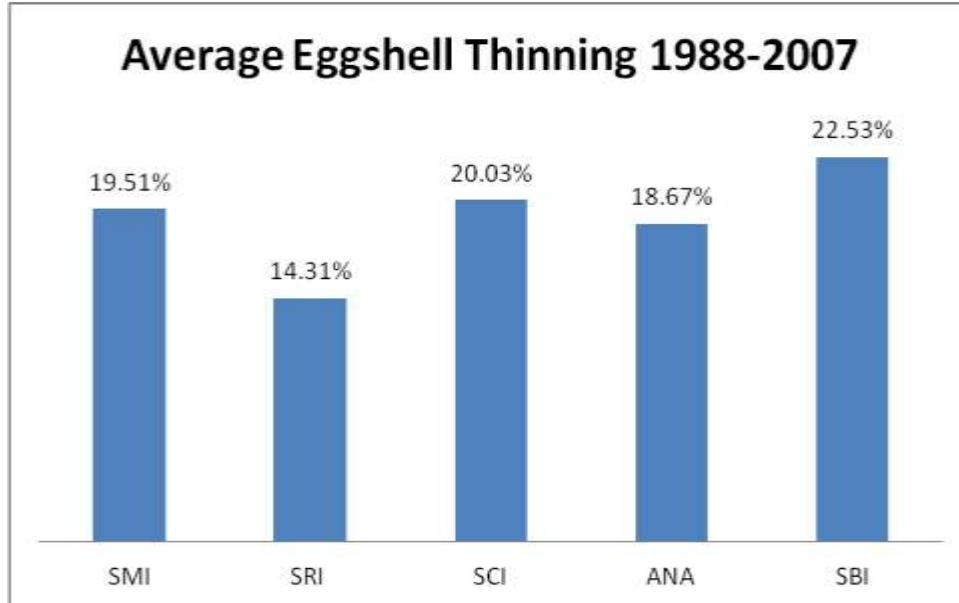
**Figure 11. Percent Eggshell Thinning on the Channel Islands, 1988-2007.**



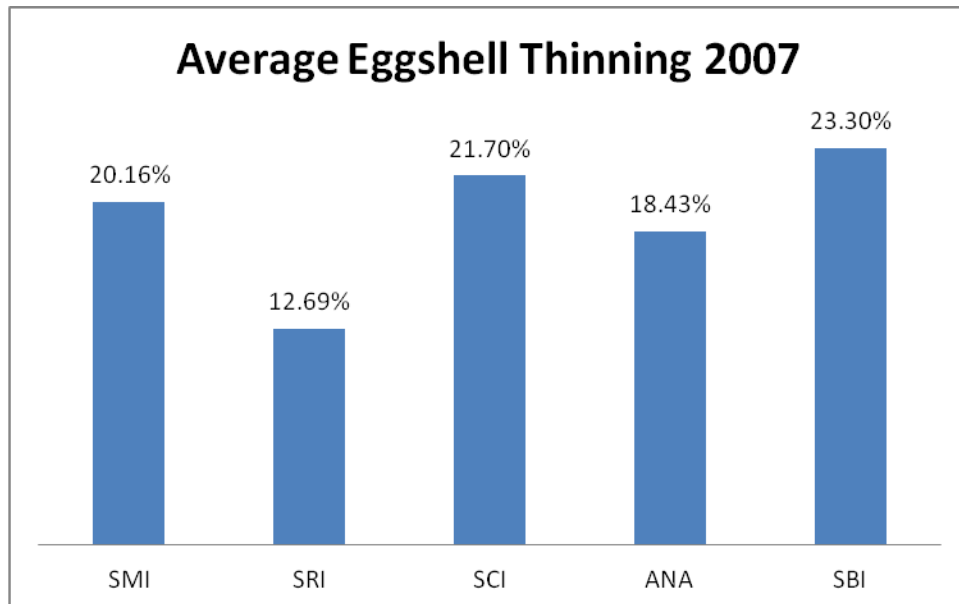
While this apparent trend is encouraging, it is somewhat misleading. Of the 53 individual clutch samples collected since 1988, the two with the highest percentage of thinning (33.24%, 29.18%) were laid in 2003, the next two highest (28.72%, 26.71%) were laid in 2007, 15 and 20 years after the recovery began. Clearly, our results indicate a high degree of continuing DDE contamination and its resultant effects on eggshell thickness and productivity on the majority of the islands in the archipelago.

Eggshell thinning varies from island to island. Kruskal-Wallis One-way Analysis of Variance of eggshell thickness measurements from the three islands with comparably large sample sizes (San Miguel, Santa Rosa, and Santa Cruz) show this variation to be significant for all years combined ( $p=0.000$ ,  $df=2$ ) as well as for pre-2007 samples only ( $p=0.001$ ,  $df=2$ ). San Miguel, Santa Cruz, Anacapa and Santa Barbara Islands have consistently averaged over 18.5% thinning, while Santa Rosa has experienced levels below 17% (Figure 12). In 2007, eggshell thinning levels were higher than the overall average for San Miguel, Santa Cruz, and Santa Barbara, only slightly lower than the average for Anacapa (Figure 13). Santa Rosa, meanwhile has shown a marked improvement in eggshell thickness.

**Figure 12. Average Eggshell Thinning by Island from 1988-2007.**



**Figure 13. Average Eggshell Thinning by Island for 2007.**

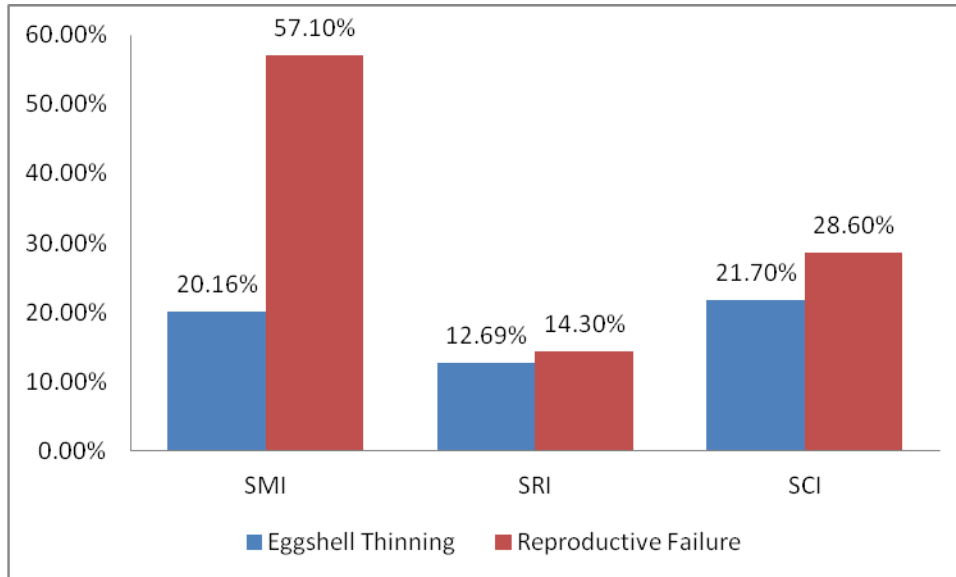


Productivity in 2007 (1.46 young per active pair) was lower than that reported by Hunt (1994) for 1993 (1.71) but higher than for 1994 (1.21). Likewise, Percent Failure for the islands combined in 2007 (33.3%) lies between the values for 1993 (28.6%) and 1994 (37.5%).

The variability seen in eggshell thinning on a per island basis is also apparent in the productivity data. In 2007 Percent Failure corresponded with the levels of eggshell thinning on three of the five islands with active peregrine territories. San Miguel and Santa Cruz Islands averaged 20.16% and 21.70% thinning and had correspondingly high percentages of reproductive failure

(57.1% and 28.6%). Santa Rosa Island had comparatively low percentages of both thinning (12.69%) and reproductive failure (14.30%) (Figure 14). Anacapa and Santa Barbara Islands with their small sample sizes of one active territory each were left out of the comparison.

**Figure 14. Comparison of Eggshell Thinning v. Reproductive Failure on San Miguel, Santa Rosa, and Santa Cruz Islands 2007.**

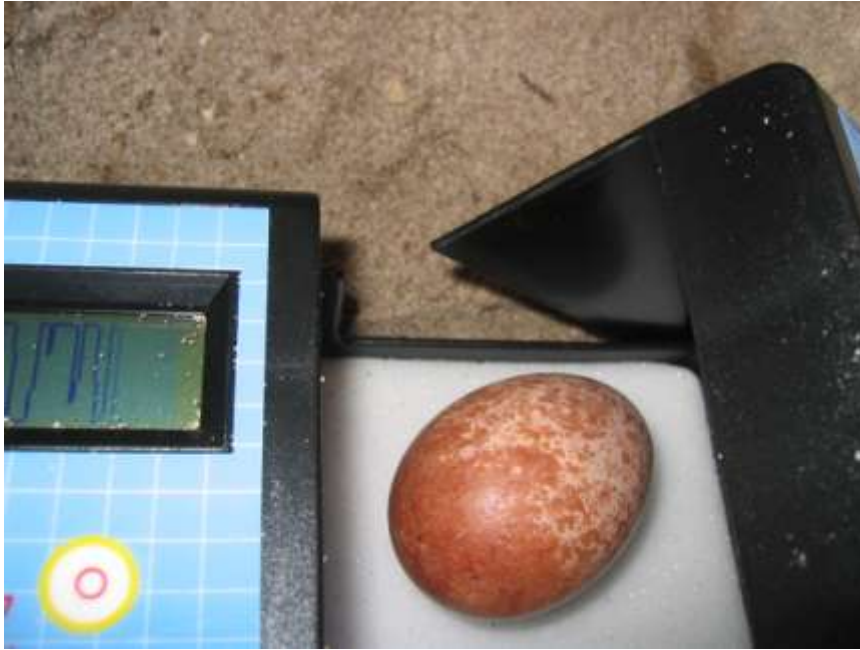


While continuing levels of eggshell thinning in excess of 17% may be repressing productivity on the Channel Islands as a whole, Santa Rosa Island has averaged less than 17% thinning since recovery began in the late 1980s and experienced greater than 85% reproductive success in 2007 accounting for 43% of the total productivity on the islands.

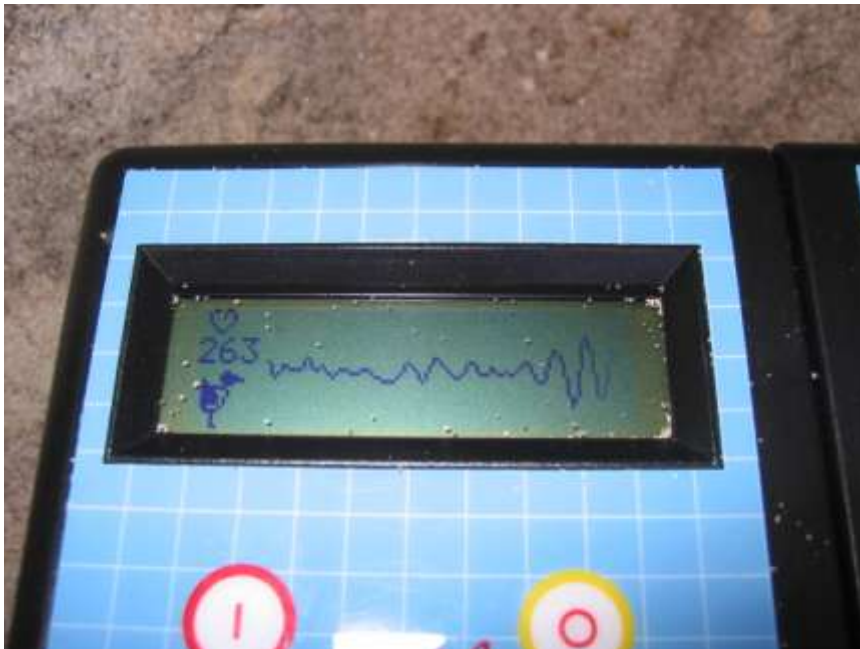
### **Addled Eggs**

We tested six peregrine eggs at three different eyries (Santa Barbara Is., East Anacapa, and SMI Carbon) using the Buddy™ digital egg monitor. When an egg was placed on the sensor pad in the sound chamber, the Egg Buddy amplifies the cardiovascular sounds from inside the egg and gives a digital readout of the embryonic heart rate and linear pulse rate graph (Figures 15 and 16). All six eggs selected in the nest sites were viable (i.e., alive) at the time of testing, and therefore not collected. The four eggs tested at Santa Barbara Island and East Anacapa subsequently hatched. The two eggs at SMI Carbon did not hatch and we collected one egg intact after the adults abandoned the nesting attempt. The other egg broke in the nest while being incubated by the adult.

**Figure 15. Buddy™ Digital Egg Monitor with peregrine falcon egg from SMI Carbon Point.**



**Figure 16. Buddy™ Digital Readout of Live Peregrine Falcon Egg from SMI Carbon Point.**



Latta and Pagel collected three other addled eggs by chance from three different eyries (SRI Trancion, SRI Bee Rock Canyon 1, and SRI Bee Rock Canyon 2) during banding and sample climbs. While entering nest sites early to collect eggs appears the best way to collect eggs prior

to breakage, it is unclear from our experience whether or not testing egg viability during incubation with a digital egg monitor can be a more efficient method of collecting added eggs for analysis. The sample size was small and more testing is needed.

### Contaminant Levels and Eggshell Thinning

DDE wet weight values of 15-20 ppm (parts per million) in peregrine falcon eggs have been shown to represent the critical level at which eggshells become more than 17 percent thin and populations decline (see Peakall and Kiff 1988, Peakall *et al.* 1990, Fyfe *et al.* 1988). The wet weight geometric mean DDE value of the 4 peregrine eggs collected on the Channel Islands in 2007 was 9597 µg/kg (9.5 ppm), well below the threshold contamination level for adverse effects. This appears to indicate a marked improvement from the 19.6 ppm mean wet weight DDE value found in 16 peregrine eggs collected from the Channel Islands in 1992 by Hunt (1994). However, our sample size of four is small and three of those eggs were collected on Santa Rosa Island, which has the lowest average eggshell thinning of all the islands where samples were collected from 1988 to 2007 (Tables 8 and 9). Contaminant levels as well as percent thinning measured in the eggs collected from Santa Rosa Island were much lower than that of the egg collected from San Miguel Island (Table 15). San Miguel Island has consistently averaged over 18% eggshell thinning since 1999. The DDE level of the SMI Carbon egg of 57900 µg/kg (57.9 ppm) is higher than 15 of the 16 eggs (range 7.1 to 69.6 ppm) from Hunt's 1994 study, making it the 2<sup>nd</sup> highest DDE contaminated peregrine egg ever collected from the Channel Islands. Despite the relatively small sample size this analysis indicates a high degree of continuing contamination in parts of the Channel Islands ecosystem.

**Table 15. Eggshell Thinning, DDE and PCB wet weight values (µg/kg) for 4 Channel Islands Peregrine eggs collected in 2007.**

Sample	Eyrie	% Thinning	DDE	Total PCBs
MC-57	SMI Carbon Pt	22.5	57900	13255
MC-34-1	SRI Bee Rock Cyn 1 (2007)	16.65	4220	675
MC-34-2	SRI Bee Rock Cyn 2 (pre-2007)	14.04	2650	496
MC-50	SRI Trancion	1.51	13100	3870

Analysis of PCB levels also shows the egg from SMI Carbon to be the most contaminated of the 2007 samples. The wet weight total PCBs value for this egg (13255 µg/kg) is higher than those found in an analysis of seven mainland California eggs collected in the 1980s (Jarman *et al.* 1993). The SMI Carbon egg also contained higher levels of two non-*ortho* PCBs 77 and 169 (4.66 and 0.45 µg/kg respectively) than the eggs in Jarman's study. These two are among the most toxic of PCB congeners (McKinney *et al.* 1976, Brunström and Darnerud 1983, Van den Berg *et al.* 1998).

Exposure to PCBs has been associated with a number of sensitive reproductive effects in birds. Embryo lethality and deformities are common and sensitive adverse effects associated with *in ovo* exposure to PCBs, and dietary exposure to PCBs has been associated with abnormal nesting behavior, including poor eyrie attentiveness and abandonment (Harris and Elliott 2011). Field and laboratory studies have related concentrations of total PCBs and two specific congeners (77 and 126) in raptor eggs to effects on embryos and on parental behavior (where the concentration in the egg is a measure of exposure by the female parent; Harris and Elliott 2011).

Thresholds for PCB-related embryo lethality are based on concentrations of dioxin-like PCB congeners 77 and 126. The concentrations of PCB 77 measured in the 2007 peregrine eggs ranged from approximately 0.32 – 4.7 µg/kg ww (wet weight), and as such were well below threshold the threshold of 316 µg/kg

suggested by Harris and Elliott (2011). Similarly, concentrations of PCB 126 ranged from  $<0.02 - 0.32 \mu\text{g/kg}$  and as such are well below the threshold of  $65 \mu\text{g/g}$  suggested by Harris and Elliott (2011) for embryo lethality in raptors. PCBs 126 and 77 are among a number of congeners with dioxin-like toxicity. The potential for all of the dioxin-like congeners to cause embryo lethality was not evaluated here.

However, it is noted that along with PCB congeners 81 and 169, PCBs 126 and 77 are among the most potent (i.e., likely to exert adverse effects). The potency of PCB congener 81 is equal to that of PCB 126, while the potency of PCB 169 is one-tenth that of PCB 126. Concentrations of PCB 81 were all  $<0.07$ , and concentrations of PCB 169 were  $<0.04-0.45 \mu\text{g/kg}$ , indicating that concentrations of PCB 81 and 169 would also be below levels of concern.

Concentrations of total PCBs measured in the falcon eggs ranged from approximately  $500 - 13,700 \mu\text{g/kg}$  with the most contaminated egg coming from the San Miguel Island eyrie (Table 2). While the total PCB concentration in the San Miguel Island egg could be considered elevated, it does not exceed thresholds suggested by Harris and Elliott (2011) for impacts on hatching or fledging success ( $35,000 \mu\text{g/kg}$ ) or productivity of multiple years ( $25,000 \mu\text{g/kg}$ ) in raptors.

### **Prey Remains and Eggshell Thinning**

Prey remains collected in 2007 represent the spring diet of breeding peregrines. The results of our analysis are relatively consistent with that reported by Hunt (1994) in that seabirds represented the largest proportion of the diet by biomass. The spring diet in 1992-93 consisted of 54% seabirds, 8% shorebirds, and 38% land birds in terms of biomass. The 2007 collective spring diet consisted of 72% seabirds, 7% shorebirds, and 21% land birds. Our results are also consistent with Hunt's in that gulls and alcids make up the largest portion of the spring diet. We can therefore assume that winter diets of 2007 and 1992-93 are also similar. The winter diet is consumed when female peregrines are in the process of forming eggs and contaminants carried by those prey species can affect eggshell thickness and structure. Hunt (1994) found that "that local seabirds, mainly gulls and auklets, are the primary source of DDE to the peregrines through the food chain," and that the DDE levels of these species were "sufficient to explain the observed rates of DDE contamination and thinning of peregrine eggs" on the Channel Islands. Given that diets are relatively similar, we can only infer that local gulls and auklets are still the primary vector for DDE contamination in Channel Islands peregrines and are responsible for the observed eggshell thinning in 2007 (Figure 17). No sampling of prey for DDE levels was conducted during this study.



**Figure 17. Western gull partially consumed by a Peregrine Falcon on Santa Barbara Island in 2007. (photo B. Latta)**



It is interesting to note that rock doves, which made up the highest proportion of the 1992-93 of the spring diet biomass (12.7%) for a single species, are completely absent from the 2007 samples. This may be due to rock dove control measures instituted by the Park Service on Santa Rosa Island were they had become established as a breeding species. While rock doves carry relatively low loads of DDE (Cade and Bird 1990), they only constituted 3.6% of the 1992-93 winter diet (Hunt 1994) and therefore were not likely to significantly affect levels of eggshell thinning.

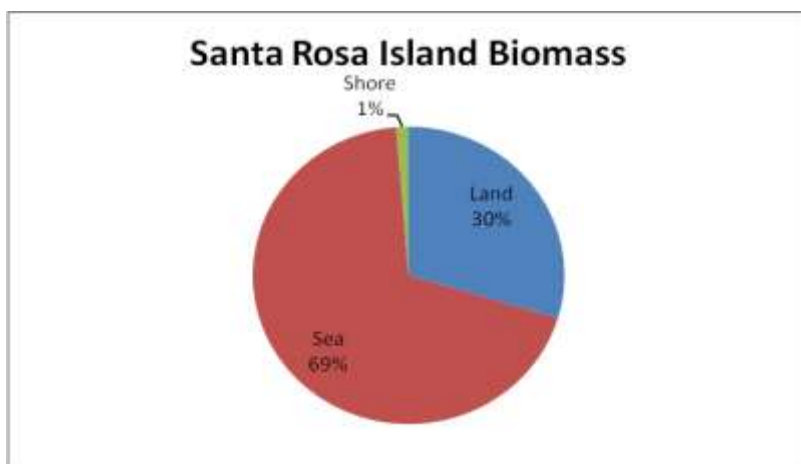
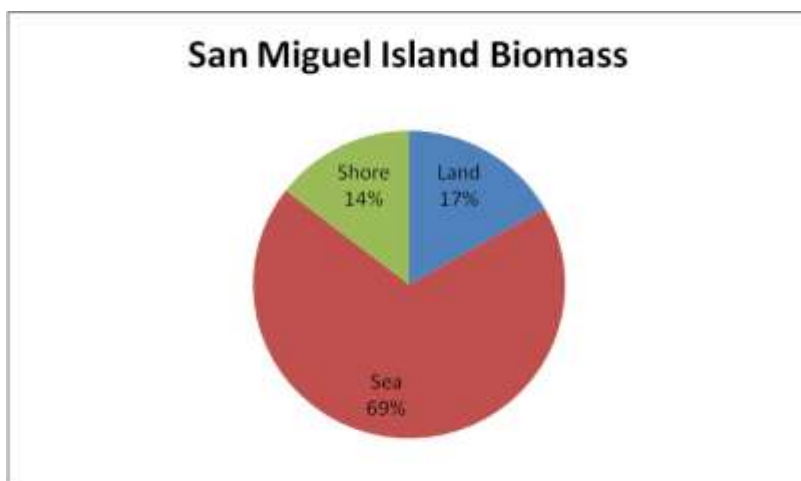
While it would be of interest to compare the composition of prey remains collected at each eyrie to the eggshell thinning and contamination levels specific to those eyries, the individual eyrie sample sizes were insufficient to make that comparison in a meaningful way. In addition, the eyries that failed did not contain prey remains because there were no nestlings to be fed. However, with the assumption that each island's cohort of peregrines have access to the same prey species residing on and around those specific islands, the sample sizes are sufficient to make a meaningful comparison of the combined prey remains samples for each island with the average of the clutch means (average eggshell thinning per eyrie) for each corresponding island.

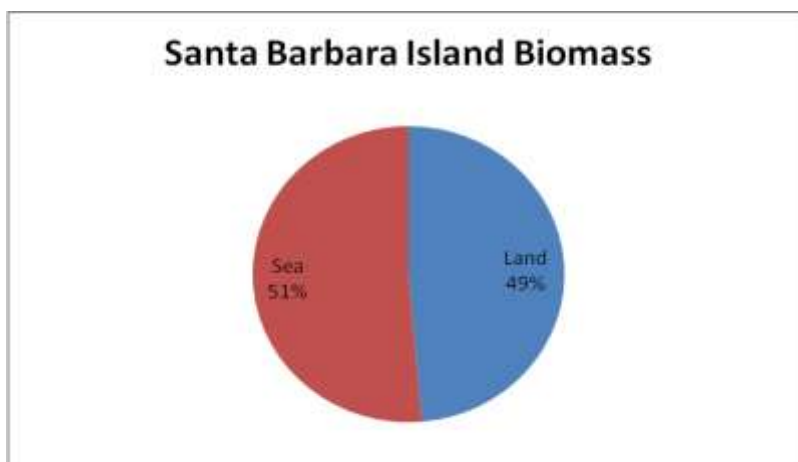
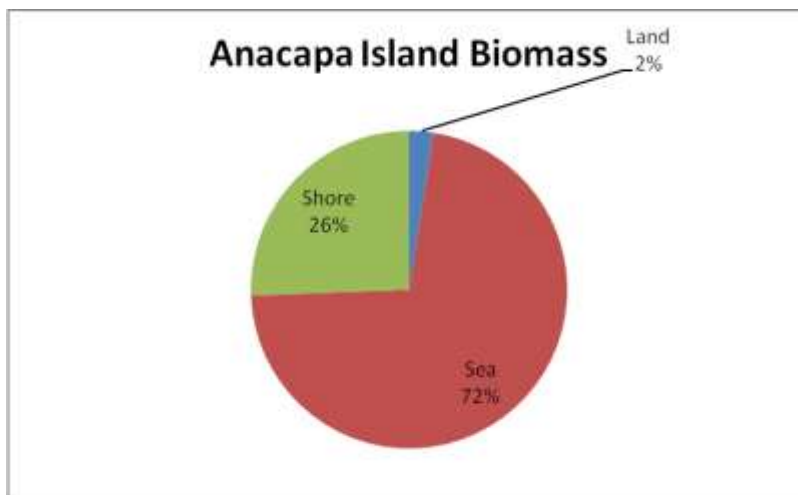
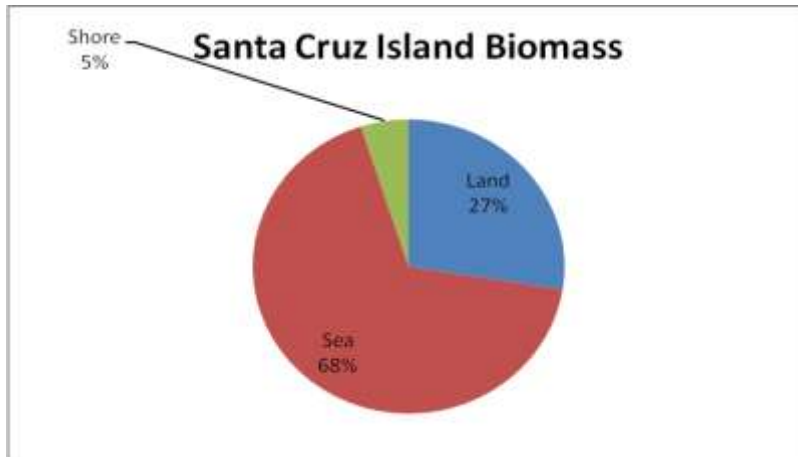
The 2007 spring diet, as determined by our prey remains analysis, did contain a higher percentage by weight of sea birds (aquatic foragers) than land or shore birds (terrestrial or shoreline foragers) on both a collective and per island basis. However, this analysis does not appear to account for the variability in eggshell thinning or productivity between the individual islands. Santa Rosa Island, with an average eggshell thinning of 12.69% consumed a higher percentage by weight of aquatic foraging prey (69%) than did Santa Barbara Island (51%), which had significantly higher eggshell thinning at 23.30% (Table 16). Anacapa Island, which had the second lowest percentage of eggshell thinning (18.43%), consumed the second highest percentage by biomass of aquatic foragers (72%).

**Table 16. Eggshell Thinning compared to Percentage of Biomass of Spring Diet by Island in 2007.**

Island	Eggshell Thinning	Percent Biomass		
		Sea birds	Land birds	Shore birds
SMI	20.16%	69%	17%	15%
SRI	12.69%	69%	30%	1%
SCI	21.70%	68%	27%	5%
ANA	18.43%	72%	2%	26%
SBI	23.30%	51%	49%	0%
Collective	18.34%	69%	23%	8%

Clearly, there is no correlation apparent between the compositions of the 2007 spring diet for each island (Figure 18) and the eggshell thinning reported in the table above.

**Figure 18. Percent Biomass per Habitat Type of the 2007 Spring Diet by Island.**



An intensive analysis of the winter diet on each island combined with an extensive contaminant analysis of the species that compose the winter diet, as was conducted by Hunt (1994), would be a better strategy for determining not only the causes of the variability in eggshell thinning and productivity between islands demonstrated by this study but also the extent of continuing DDE contamination in the archipelago as a whole.

## CONCLUSIONS

The recovering subpopulation of American peregrine falcons on the Channel Islands has exceeded the known historic population and is nearing the carrying capacity on the northern islands predicted by Hunt (1994). Re-establishment on the southern islands has not been as successful though more thorough surveys are warranted on San Nicholas and San Clemente Islands.

Analysis of peregrine falcon eggshell thinning has shown a trend towards improvement (i.e., thicker eggshells) over time since re-establishment began on the Channel Islands in the mid-1980s. However, the current levels of eggshell thinning still exceeds the 17 percent threshold characteristic of declining populations as reported by Peakall and Kiff (1988) and the 15 percent threshold regarded as injurious under Department of the Interior Natural Resources Damage Assessment Regulations. The four highest levels of eggshell thinning ever recorded from Channel Islands peregrines were laid in recent years (2003 and 2007) indicating a persistence of DDE contamination at high levels in the archipelago.

Eggshell thinning levels have been shown to vary among islands. Three of the five islands with active peregrine falcon pairs continue to have levels of thinning over 20% and two of these, San Miguel and Santa Cruz Islands, have correspondingly low reproductive success. Only Santa Rosa Island has an average eggshell thinning below the 17% threshold and it accounted for over 40% of the total productivity for the islands.

Seabirds continue to constitute the majority of the peregrine falcon diet during the nesting period and are likely still the major contributor in the continued DDE contamination and resultant eggshell thinning in Channel Islands peregrines. However, analysis of the 2007 spring diet failed to show a correlation between diet composition and eggshell thinning or reproductive failure, indicating that an analysis of the fall and winter diet is warranted to better determine the sources of eggshell thinning variability among the islands.

Long-term monitoring will be necessary to accurately assess the trends in the on-going recovery of the peregrine falcon; extensive sample collection will be necessary for noting trends in source-sink population demography on the islands and documenting changes in site-specific contaminant levels through time.

## **RECOMMENDATIONS**

We recommend that monitoring and sample collection on the Channel Islands be continued every 2 to 3 years in order to accurately assess and document peregrine falcon recovery and the long term effects of organochlorine contaminants.

We also recommend that archived contaminant samples be analyzed and seabirds represented in the peregrine's fall and winter diet be collected for contaminant analysis in order to more accurately compare current data to past studies and determine the trends and pathways of DDE contamination in the Channel Islands food chain.

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## APPENDICES

### **Appendix i. Excerpt from *Guide to Management of Peregrine Falcons at the Eyrie*, T.J. Cade, J.H. Enderson, and J. Linthicum, eds., 1996. The Peregrine Fund.**

#### **Observing Breeding Behavior** **Janet Linthicum**

It is important that suspected nesting areas be adequately checked, especially early in the breeding season. In areas where reproductive success is being monitored, all territories should be checked at least twice during the nesting season. More frequent visits may be necessary to determine exact timing or outcomes if precise information is needed, for example in manipulation efforts. Visits are usually most productive if they occur at dawn or dusk, because behaviors such as food and nest exchanges are highly likely to occur at these times. During other parts of the day, more time may be required at a site to get the same information.

All sites should be documented in such a way that a later researcher can easily find them. Directions to the site, photographs, and sketches are all extremely helpful, and should be put on file (confidentially) in case the current researcher is not available for future survey work.

#### **Timing**

**Incubation.** Mid-March (April or later in northern areas or high elevations). Determine whether the territory is occupied by one or two falcons. Record presence of falcons, age, courtship, incubation behavior, nest location, band status, etc. If no falcons are seen, the site should be visited again, and possible alternate sites checked, as Peregrines can be very hard to detect during incubation. First-time layers often lay eggs later than expected for their region. Incubation lasts approximately 33 days.

**Nestlings.** Late April to June in temperate latitudes. Determine whether adults are still attending the nest where eggs were laid, and whether young have hatched. If there is nest failure, the pair may have relocated and laid another clutch on a different ledge. If it is possible to see into the nest from the observation point, record the number of young.

**Fledging.** Late May to mid-August. Depending on previous nest chronology, young should be ready to fly near this time, roughly 40 days after hatching. Recycling after egg failure can cause nest departure to be delayed from the “expected” date by a month or more. Record number and sex of fledged or near-fledged young. At sites where the observer cannot see into the nest, young must be counted after fledging. The resulting number should be considered a minimum, as some young could go undetected or have died or dispersed before the visit.

#### **Behavior**

This information is intended to help in determining reproductive status at eyries where the observer cannot see into the nest, and so must ascertain status based on behavior. It is written primarily for those watching nests intensively, for example if manipulation is planned, but may also be useful for individuals with limited experience. It is helpful if observers use this information to describe vocalizations and behaviors in a standardized way. For example, reports of Peregrines “peeping” or “calling” do not convey useful information to the reader. Detailed descriptions of behavior can be found in Cramp and Simmons (1980), Sherrod (1983), and Ratcliffe (1993).

**Courtship. BOWING.** A general display used in many situations, especially as part of courtship.

**MALE OR FEMALE LEDGE DISPLAY.** The falcon stands over the nest depression (scrape), leaning forward (bowing) and ee-chupping. The male often stares at the female during a male ledge display. Ledge displays are often accompanied by;

**SCRAPING.** Either bird can do this. The falcon runs its breast through the substrate or nest depression, pushing out with its legs behind. The bird is forming the nest cup (scrape), but this is also part of courtship. Scrapes may be made at several potential ledges before one is finally chosen for laying.

**MUTUAL LEDGE DISPLAY.** Often this is precipitated by a male or female ledge display. The other bird joins the first on the ledge and both bow and ee-chup over the scrape, sometimes touching bills. This can also happen outside the eyrie.

**FOOD TRANSFER.** The male offers food to the female by approaching her or standing near, with food in talons or beak, ee-chupping. The female takes the food from the male, usually ee-chupping or wailing. This can happen in the air or perched. The male often signals the female that he has food by wailing as he approaches the cliff.

**LANDING DISPLAY AND HITCH-WING POSTURE.** (male). A pre-copulatory display in which “shoulders” are held high, as if in a shrug, and male often prances as if on tip-toe.

**COPULATION.** The female leans forward and moves her tail to one side. The male rests on his tarsi on her back, flapping his wings, and presses his tail underneath the female’s. Copulations are usually accompanied by wailing on the female’s part, and chittering or ee-chupping by the male. When the male departs, the female usually ee-chups a few times, and often rouses (shakes her feathers).

**Other behaviors. CACHING.** Peregrines sometimes store uneaten food for later retrieval. They usually have several favorite cache spots on the cliff or elsewhere in the territory.

**CASTING.** The falcon hangs its head and wags it from side to side with mouth open. Eventually a pellet (casting) of non-digestible material is expelled.

**Vocalizations. EE-CHUP.** A repetitious, staccato ee-chup ee-chup ee-chup sound. Males have a higher-pitched “eechip”. Variations include a slower chip chip chip, usually during ledge displays and while feeding young. Ee-chup usually implies social recognition, but a very similar sound, louder and more staccato, is given as a response to vagrant raptors, usually Peregrines.

**CAcking.** Very loud cack cack cack -- A response to disturbance, either a raptor or other animal (including the observer) too near the eyrie.

**WAILING.** A long, slow, ascending waaaaaa waaaaaa waaaaa. Sometimes connotes hunger, but also used in a variety of circumstances. Youngsters have a more insistent variation of this call, which is often referred to as hunger screaming.

**CHITTERING.** Like ee-chupping but quicker and less defined. Usually used by birds in proximity, often when one bird is being made uncomfortable by some aspect of the interaction, or during play by fledglings.

## **Behavioral Chronology**

**Pre-Laying.** Both birds are visible for extended periods outside the nest. This can happen when there is a partial clutch.

**PAIR FLYING.** Both birds engage in high speed acrobatic displays, with no apparent hunting or territoriality involved. This indicates that the female is probably not lethargic with eggs yet. Sometimes males engage in spectacular flight displays while the female watches.

**TANDEM HUNTING.** Self-explanatory. Again, the female is probably not laying eggs yet.

**LEDGE DISPLAYS.** See above. **NOTE:** Sometimes the falcons concentrate courtship in one spot, then suddenly lay eggs in a different, often more cryptic location. If both birds are suddenly no longer seen together, or activity at the expected nest subsides, suspect that the birds have moved and that they might have eggs.

**FOOD TRANSFERS.** These occur, male to female, in the air or at a perch throughout the nesting season. As incubation approaches, concentrate on the male after the transfer. He is often the key to incubation as described later.

**COPULATION.** Before and during egg laying, Peregrines copulate frequently. When the clutch is complete they rarely copulate.

**Egg-Laying. LETHARGY.** Just before and during the period of egg laying (approximately eight days for four eggs) the female becomes lethargic. She can look “dumpy”, including fluffed-up feathers while perched, hanging her vent feathers (the feathers in front of the cloaca, underneath the tail) to an unusual degree, leaning slightly forward while perched, waddling when walking, dozing with one or both eyes closed for long periods, and generally remaining near the nest and being inactive. She might also spend considerable amounts of time in the nest by herself. After laying an egg, she may have periods of being more active, but lethargy is a general demeanor to note. Those without much previous experience with Peregrines should be aware it is comparative and subjective.

**PARTIAL CLUTCH.** The falcons usually begin incubating after the second or third egg, even if a fourth is to be laid. Before incubation starts, they often “guard” the eggs, standing in the nest or within sight of the eggs. This is an indication that at least something is in there. Again, the male is the key. After a food transfer or nest exchange, watch the male. If he enters the nest for a while (even a long while) then comes out and perches out of the nest while the female also remains outside, you are fairly safe in assuming that full incubation has not started.

**Incubation.** During the normal course of incubation, one of the adults is nearly always on the nest. Exceptions are during disturbance, for short periods on particularly warm days, or for a few minutes during food exchanges. The female does the majority of incubation. The male brings food to her several times daily, or sometimes simply relieves her and takes a turn on the eggs while the female eats, preens, and relaxes. When she returns to the nest to relieve the male, he usually appears on the ledge when she disappears; an unaware observer may think only one bird was involved in a brief visit to the ledge. A common mistake is failure to realize that the bird leaving a spot is not the same bird that just arrived there (i.e., nest exchange as opposed to just perching briefly). This is why it is important to be able to distinguish sexes. During food exchanges the male arrives with food, often wailing or ee-chupping and passing in front of the eyrie where the female can see him. She then exits the eyrie and takes the food, either at a perch or in the air. This exchange gives a good opportunity for locating the nest. The best way to determine that incubation is occurring is to train your attention intently on the eyrie and be certain that the attending falcon remains in the nest until relieved by the other adult. This can be very tedious, but is worth the trouble because otherwise it is possible to see a lot of behavior, and yet not determine what is happening. Observation of several sequences in which an adult attends until a nest exchange occurs indicates that incubation is underway.

If the observer is unable to see the eyrie opening, other behaviors may be helpful. For example, **VOLUMINOUS EXCRETION** has been used to determine incubation in coastal California, where the observer sometimes cannot see the cliff face that the eyrie is on. When a nest exchange is occurring (e.g., the male brings in food and disappears toward the nest, and soon thereafter the female appears coming from that area) watch the female. After she perches, she soon

slowly leans forward and emits a large quantity of excreta. This can also occur while flying. This behavior indicates that the falcon has been unable to defecate for a prolonged time (i.e., has been incubating). Also watch for rousing (shaking of all feathers in a relaxing manner), stretching, and preening intensively. All of these are normal behaviors, but tend to be exaggerated after a stint of incubation.

**Egg Failure.** Some pairs lose their eggs to breakage, weather, or other factors. If this occurs while laying is still underway, they may relocate to a different ledge and attempt to complete the clutch there. If the clutch has been completed and incubation is underway, and the eggs are then lost, the first egg of the second clutch is usually laid approximately fourteen days later if recycling occurs. Sometimes, falcons exhibit the “lost look” after failure, returning to the scrape repeatedly but not staying, and wailing frequently. The falcons usually change ledges after failure, sometimes quite a distance away (possibly an alternate cliff), so do not assume they have “given up” if they are not in the usual places. Re-nesting may occasionally occur after loss of a young brood, or even after a second set of eggs is lost.

**Young.** As hatching approaches, the adults often become more aggressive. During the early nestling stages the young require almost constant brooding, which can be hard to distinguish from incubation. The main difference is that after a food exchange, the female takes the prey into the nest rather than eating outside (she may pluck it before entering the eyrie). During the early nestling stage most females do the majority of feeding. Males provide food, and may brood young during the female’s absence.

After approximately two weeks, depending on ambient temperature and number of chicks, the young no longer need constant brooding. Therefore, both adults are often outside the nest for extended periods. This is easily mistaken for nest failure. Depending on size of prey and number of young, the nest may only be visited a few times a day by the adults. Clues to presence of young include continued territoriality by adults, absence of courtship behavior, frequent hunting attempts, sometimes hunger screams of young, and, of course, prey deliveries. As the young age, they begin eating on their own, and sometimes a prey delivery is extremely brief. Also, late in the nestling stage the female hunts, and the male as well as the female feeds young. Some males are absent from the immediate nest area most of the day, either hunting or perched out of sight, except when delivering prey. Clues to failure include either adult eating full meals without delivering food to the eyrie, decreased territoriality and presence at the cliff or resumed courtship behavior if recycling is occurring, and frequent wailing.

**Disturbance.** Observers should find an observation site with optimal visibility, but where their presence does not interfere with normal falcon behavior. In some cases distant locations can provide a better overall view of the cliff and falcons coming and going. However, those with little observation experience with Peregrines may find them difficult to spot from a distance, and vocalizations can be very helpful. The falcons respond more to an observer above the nest than to one below or across from it. Cacking birds are disturbed enough that observers should retreat and find another location immediately. Signs of lower-level disturbance can include soaring above the cliff silently (watching the observer), perching where they can watch the observer rather than engaging in normal behavior, and sometimes displacement aggression such as assaulting a cormorant, gull, or other large bird in the cliff vicinity. Generally, if a falcon seems to be watching the observer(s), they should consider retreating to a more distant location. Even if the birds are not disturbed, they may be less inclined to engage in the behavior the observer is there to see if they are distracted. Before beginning observations, find a spot from which to observe for extended periods without becoming uncomfortable, distracted, or eager to depart.

**Additional information.** Ideally, observers should learn to distinguish the male from the female, preferably while both are still visible simultaneously. The best indication of sex is size, females being larger than males. However, it can be extremely difficult to sex a single bird on this basis, and experienced observers often err. If there are identifying aspects of individual falcons, they can be very helpful once incubation has begun and the observer rarely sees both birds at once. In many pairs, the female looks darker overall on the breast and farther up toward the neck, and may have a darker, slightly brownish tinge to the back. The male looks more white on the breast from a distance, and silver on the back and especially in the rump area in flight. Some males are vividly orange around the cere (fleshy portion of beak) and feet (as opposed to bright yellow or yellowish-orange). There is much variation among individuals, so get to know the pair if possible. Male voices are higher-pitched, and in flight their wings are more narrow with “sharper” ends. Peregrines molt their flight feathers during the breeding season, with females usually beginning to molt before males. Differences in the gaps in wings and tail can be helpful in distinguishing individuals during a given day’s observation.

Occasionally one of the pair is a yearling. Yearlings have bleached considerably during the year and may appear “blond” rather than brown, and could be confused with an adult at a distance. A good method of checking is to note whether the marks on the breast are vertical streaks or horizontal bars. Occasionally, one may encounter a yearling that has already molted partially by its first spring, or a two-year-old that molted incompletely its first year. These birds may breed successfully, although many do not.

Recently fledged young are brown with vertical streaks on the front, and may appear somewhat larger than adults of the same sex, because their flight feathers are slightly longer. Their wing tips in flight are more rounded than those of adults. They often flap their wings while perched (exercise), land clumsily, and engage in mock combat, tumbling and playing together in the air. When an adult is in view, they “hunger-scream”, and often chase the adults. In begging while flying, they sometimes appear to flap their wings quickly (flutter). Seen from above, powder down may cause young in flight to appear bluish, leading to confusion with adults; however young of the year have conspicuous light tips on the tail feathers.

For future reference, notes should contain a description of the adults, especially of bands (color and leg) and any unusual characteristics if possible. This can help future observers to determine longevity, continued occupancy, etc. Some Peregrines have alpha-numeric bands in addition to U. S. Fish and Wildlife Service (USFWS) bands. These bands usually have two characters, numbers or letters or both, that are meant to be read at a distance. When one of these bands is read, it is necessary to draw the band as it appears on the leg for reporting purposes. This is because there are several combinations of the same characters in existence, and how the characters are arranged on the band is important for identifying it. For example, characters can be horizontal and/or vertical, and may have a line between them. Some bands are more than one color.

## Appendix ii. Sample Code Key and Channel Islands Sample Inventory

### Channel Islands Peregrine Study 2007 Samples

Sample ID Number Example:		07-MC33-ES-1	
		07 is the year, MC33 is the nest code, ES is sample type, 1 is sample number	
Sample ID Number Key			Sample Number
Year	Nest Code or Island Inits.	Sample Type	
07 = 2007	MC16 = SRI Carrington	ES = Eggshell (from a single egg)	1 = First sample this type collected at this location in this year
	MC17 = SMI Hoffman	EF = Eggshell fragments (from a clutch)	
	MC18 = SCI Gherini	EA = Addled Egg (whole unopened egg)	
	MC19 = SCI Laguna	(Will be separated into Eggshell and Egg Contents)	
	MC20 = SCI West End	AF = Peregrine Feather	
	MC21 = Anacapa Is (West)	CD = Chick Down	
	MC27 = SRI Lime Pt.	BC = Blood for Contaminants	
	MC27a = SRI Lime Pt. Alt. (Lobos)	BD = Blood for DNA	
	MC28 = SMI Bat Rock	BS = Blood for Stable Isotopes	
	MC30 = SCI Sea Lion	BH = Blood for General Health Assessment	
	MC31 = SRI Water Canyon	RC = Prey Remains Carcass (for contaminants)	
	MC33 = Santa Barbara Is.	RF = Prey Remains Feathers (for identification)	
	MC34 = SRI Bee Rock Canyon		
	MC35 = SRI Jaw Gulch		
	MC36 = SRI Lost Hat		
	MC37 = SMI Rat Trap		
	MC38 = SCI Black Pt.		
	MC42 = SCA Long Pt.		
	MC43 = Middle Anacapa		
	MC44 = SMI Cardwell Pt.		
	MC45 = SCI Arch Rock		
	MC46 = SCI Valley Anchorage		
	MC47 = SMI Crooked		
	MC49 = SCA Bullethead		
	MC50 = SRI Trancion		
	MC51 = SRI Krumholtz		
	MC52 = SCI Cavern		
	MC53 = SCI Bowen Pt		
	MC54 = East Anacapa		
	MC55 = SRI Soledad		
	MC56 = SRI Gnoma		
	MC57 = SMI Carbon Pt.		
	MC58 = SMI Salvador Pt.		
	MC59 = SMI Science Pt./Millenium		
	SMI = San Miguel Island		
	SRI = Santa Rosa Island		
	SCI = Santa Cruz Island		
	WAI = West Anacapa Island		
	MAI = Middle Anacapa Island		
	EAI = East Anacapa Island		
	SNI = San Nicholas Island		
	SBI = Santa Barbara Island		
	SCA = Santa Catalina Island		
	SCL = San Clemente Island		

## 2007 Channel Islands Peregrine Falcon Study Final Report

### Channel Islands Peregrine Study 2007 Biological Samples

#### ADDLED EGGS

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC57-AE-1	SMI	Carbon Pt. nest	34.05317	120.38699	Addled Egg		PEFA	9-Jun-07	B. Latta	Failed nest
2	07-MC50-AE-1	SRI	Trancion nest	33.92627	120.15704	Addled Egg		PEFA	16-May-07	J. Pagel	Successful nest
3	07-MC34-AE-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Addled Egg		PEFA	31-May-07	J. Pagel	Successful nest
4	07-MC34-AE-2	SRI	Bee R. Cyn 2006? nest	33.96691	120.19254	Addled Egg		PEFA	14-Jun-07	J. Pagel	Successful nest

#### WHOLE BLOOD

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC30-BC-1	SCI	Sealion territory	34.07294	119.88323	Whole blood	1807-28200	PEFA	23-May-07	B. Latta	Breeding adult female, trapped near nest
2	07-MC27a-BC-1	SRI	Lobos Cyn. territory	34.01244	120.09652	Whole blood	1807-96222	PEFA	13-Jun-07	B. Latta	Breeding adult female, trapped near nest

#### BLOOD IN LONGMIRE SOLUTION

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC54-BD-1	EAI	Cathedral Cove nest	34.01506	119.37112	DNA	1126-02009	PEFA	17-May-07	J. Pagel	Eyas male, only chick
2	07-MC33-BD-1	SBI	Signal Pt nest	33.47105	119.04166	DNA	1807-96326	PEFA	9-May-07	B. Latta	Eyas female, 1 of 3 chicks
3	07-MC30-BD-1	SCI	Sealion nest	34.07426	119.88335	DNA	1807-96327	PEFA	11-May-07	B. Latta	Eyas female, 1 of 3 hatched chicks, 2 chicks disappeared
4	07-MC30-BD-2	SCI	Sealion territory	34.07294	119.88323	DNA	1807-28200	PEFA	23-May-07	B. Latta	Breeding adult female, trapped near nest
5	07-MC53-BD-1	SCI	Bowen Pt. nest	33.96093	119.72368	DNA	1687-22112	PEFA	2-Jun-07	J. Pagel	Eyas female, 1 of 2 chicks
6	07-MC46-BD-1	SCI	Valley Anchorage nest	33.98623	119.6618	DNA	1126-02014	PEFA	18-Jun-07	J. Pagel	Eyas male, only chick
7	07-MC47-BD-1	SMI	Crook Pt. nest	34.02349	120.37277	DNA	2206-70064	PEFA	27-May-07	B. Latta	Eyas male, 1 of 3 chicks
8	07-MC55-BD-1	SRI	Soledad nest	34.01207	120.15848	DNA	1687-22105	PEFA	8-May-07	J. Pagel	Eyas female, 1 of 2 chicks
9	07-MC55-BD-2	SRI	Soledad nest	34.01207	120.15848	DNA	1697-22104	PEFA	8-May-07	J. Pagel	Eyas female, 1 of 2 chicks
10	07-MC51-BD-1	SRI	Krumholtz nest	33.90104	120.12849	DNA	1126-02008	PEFA	15-May-07	J. Pagel	Eyas male, 1 of 3 chicks
11	07-MC51-BD-2	SRI	Krumholtz nest	33.90104	120.12849	DNA	1687-22106	PEFA	15-May-07	J. Pagel	Eyas female, 1 of 3 chicks
12	07-MC16-BD-1	SRI	Carrington Pt. 07 nest	34.03597	120.05762	DNA	1687-22109	PEFA	30-May-07	J. Pagel	Eyas female, 1 of 2 chicks
13	07-MC34-BD-1	SRI	Bee R. Cyn Pinnacle 07	33.96681	120.19307	DNA	1687-22110	PEFA	31-May-07	J. Pagel	Eyas female, 1 of 3 chicks

## 2007 Channel Islands Peregrine Falcon Study Final Report

			nest								
14	07-MC27a-BD-1	SRI	Lobos Cyn. territory	34.01244	120.09652	DNA	1807-96222	PEFA	13-Jun-07	B. Latta	Breeding adult female, trapped near nest
15	07-MC27a-BD-2	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	DNA	1687-22114	PEFA	14-Jun-07	J. Pagel	Eyas female, 1 of 3 chicks
16	07-MC50-BD-1	SRI	Trancion nest	33.92627	120.15704	DNA	1687-22108	PEFA	16-May-07	J. Pagel	Eyas female, 1 of 2 chicks

### WHOLE BLOOD

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC54-BS-1	EAI	Cathedral Cove nest	34.01506	119.37112	Stable Isotope.	1126-02009	PEFA	17-May-07	J. Pagel	Eyas male, only chick
2	07-MC33-BS-1	SBI	Signal Pt nest	33.47105	119.04166	Stable Isotope.	1807-96326	PEFA	9-May-07	B. Latta	Eyas female, 1 of 3 chicks
3	07-MC30-BS-1	SCI	Sealion nest	34.07426	119.88335	Stable Isotope.	1807-96327	PEFA	11-May-07	B. Latta	Eyas female, 1 of 3 hatched chicks, 2 chicks disappeared
4	07-MC30-BS-2	SCI	Sealion territory	34.07294	119.88323	Stable Isotope.	1807-28200	PEFA	23-May-07	B. Latta	Breeding adult female, trapped near nest
5	07-MC53-BS-1	SCI	Bowen Pt. nest	33.96093	119.72368	Stable Isotope.	1687-22112	PEFA	2-Jun-07	J. Pagel	Eyas female, 1 of 2 chicks
6	07-MC46-BS-1	SCI	Valley Anchorage nest	33.98623	119.6618	Stable Isotope.	1126-02014	PEFA	18-Jun-07	J. Pagel	Eyas male, only chick
7	07-MC47-BS-1	SMI	Crook Pt. nest	34.02349	120.37277	Stable Isotope.	2206-70064	PEFA	27-May-07	B. Latta	Eyas male, 1 of 3 chicks
8	07-MC55-BS-1	SRI	Soledad nest	34.01207	120.15848	Stable Isotope.	1687-22105	PEFA	8-May-07	J. Pagel	Eyas female, 1 of 2 chicks
9	07-MC55-BS-2	SRI	Soledad nest	34.01207	120.15848	Stable Isotope.	1697-22104	PEFA	8-May-07	J. Pagel	Eyas female, 1 of 2 chicks
10	07-MC51-BS-1	SRI	Krumholtz nest	33.90104	120.12849	Stable Isotope.	1126-02008	PEFA	15-May-07	J. Pagel	Eyas male, 1 of 3 chicks
11	07-MC51-BS-2	SRI	Krumholtz nest	33.90104	120.12849	Stable Isotope.	1687-22106	PEFA	15-May-07	J. Pagel	Eyas female, 1 of 3 chicks
12	07-MC16-BS-1	SRI	Carrington Pt. 07 nest	34.03597	120.05762	Stable Isotope.	1687-22109	PEFA	30-May-07	J. Pagel	Eyas female, 1 of 2 chicks
13	07-MC34-BS-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Stable Isotope.	1687-22110	PEFA	31-May-07	J. Pagel	Eyas female, 1 of 3 chicks
14	07-MC27a-BS-1	SRI	Lobos Cyn. territory	34.01244	120.09652	Stable Isotope.	1807-96222	PEFA	13-Jun-07	B. Latta	Breeding adult female, trapped near nest
15	07-MC27a-BS-2	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	Stable Isotope.	1687-22114	PEFA	14-Jun-07	J. Pagel	Eyas female, 1 of 3 chicks
16	07-MC50-BS-1	SRI	Trancion nest	33.92627	120.15704	Stable Isotope.	1687-22108	PEFA	16-May-07	J. Pagel	Eyas female, 1 of 2 chicks

### PEREGRINE FEATHERS

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC54-CD-1	EAI	Cathedral Cove nest	34.01506	119.37112	Down	1126-02009	PEFA	17-May-07	J. Pagel	Eyas male, only chick
2	07-MC33-CD-1	SBI	Signal Pt nest	33.47105	119.04166	Down	1807-96326	PEFA	9-May-07	B. Latta	Eyas female, 1 of 3 chicks
3	07-MC30-CD-1	SCI	Sealion nest	34.07426	119.88335	Down	1807-96327	PEFA	11-May-07	B. Latta	Eyas female, 1 of 3 hatched chicks, 2 chicks disappeared



## 2007 Channel Islands Peregrine Falcon Study Final Report

4	07-MC30-AF-1	SCI	Sealion territory	34.07294	119.88323	Adult feather	1807-28200	PEFA	23-May-07	B. Latta	Breeding adult female, trapped near nest, molted primary
5	07-MC30-AF-2	SCI	Sealion territory	34.07294	119.88323	Adult feather	1807-28200	PEFA	23-May-07	B. Latta	Breeding adult female, trapped near nest, clipped breast feathers(2)
6	07-MC53-CD-1	SCI	Bowen Pt. nest	33.96093	119.72368	Down	1687-22112	PEFA	2-Jun-07	J. Pagel	Eyas female, 1 of 2 chicks
7	07-MC53-AF-1	SCI	Bowen Pt. nest	33.96093	119.72368	Adult feather		PEFA	2-Jun-07	J. Pagel	Molted adult primary
8	07-MC53-AF-2	SCI	Bowen Pt. nest	33.96093	119.72368	Adult feather		PEFA	2-Jun-07	J. Pagel	Molted adult contour feather
9	07-MC46-CD-1	SCI	Valley Anchorage nest	33.98623	119.6618	Down	1126-02014	PEFA	18-Jun-07	J. Pagel	Eyas male, only chick
10	07-MC46-AF-1	SCI	Valley Anchorage nest	33.98623	119.6618	Adult feather		PEFA	18-Jun-07	J. Pagel	Molted remidge from nest
11	07-MC47-CD-1	SMI	Crook Pt. nest	34.02349	120.37277	Down	2206-70064	PEFA	27-May-07	B. Latta	Eyas male, 1 of 3 chicks
12	07-MC47-AF-1	SMI	Crook Pt. nest	34.02349	120.37277	Adult feather		PEFA	27-May-07	B. Latta	Molted adult secondary
13	07-MC47-AF-2	SMI	Crook Pt. nest	34.02349	120.37277	Adult feather		PEFA	27-May-07	B. Latta	Molted adult contour feathers
14	99-MC37-AF-1	SMI	Rat Trap 99 nest	34.0493	120.42246	Adult feather		PEFA	20-Jun-99	B. Latta	Molted contour feathers from Ad. Fem?
15	07-MC17-AF-1	SMI	Hoffman 07 nest	34.04426	120.32501	Adult feather		PEFA	12-Aug-07	J. Pagel	Moulted adult breast feather from eyrie
16	07-MC17-AF-2	SMI	Hoffman 06 nest ledge	34.04348	120.32495	Adult feather		PEFA	12-Aug-07	B. Latta	Moulted adult flight feather on ledge
17	07-MC58-AF-1	SMI	Salvador nest ledge	34.07043	120.36257	Adult feather		PEFA	13-Aug-07	J. Pagel	Moulted adult breast feather from eyrie
18	07-MC55-CD-1	SRI	Soledad nest	34.01207	120.15848	Down	1687-22105	PEFA	8-May-07	J. Pagel	Eyas female, 1 of 2 chicks
19	07-MC51-CD-1	SRI	Krumholtz nest	33.90104	120.12849	Down	1126-02008	PEFA	15-May-07	J. Pagel	Eyas male, 1 of 3 chicks
20	07-MC51-CD-2	SRI	Krumholtz nest	33.90104	120.12849	Down	1687-22106	PEFA	15-May-07	J. Pagel	Eyas female, 1 of 3 chicks
21	07-MC16-CD-1	SRI	Carrington Pt. 07 nest	34.03597	120.05762	Down	1687-22109	PEFA	30-May-07	J. Pagel	Eyas female, 1 of 2 chicks
22	07-MC34-CD-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Down	1687-22110	PEFA	31-May-07	J. Pagel	Eyas female, 1 of 3 chicks
23	07-MC27a-AF-1	SRI	Lobos Cyn. territory	34.01244	120.09652	Adult feather	1807-96222	PEFA	13-Jun-07	B. Latta	Axillary feather, clipped
24	07-MC27a-AF-2	SRI	Lobos Cyn. territory	34.01244	120.09652	Adult feather	1807-96222	PEFA	13-Jun-07	B. Latta	Axillary feather, clipped
25	07-MC27a-CD-1	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	Down	1687-22114	PEFA	14-Jun-07	J. Pagel	Eyas female, 1 of 3 chicks

### PREY REMAINS FOR IDENTIFICATION

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC54-RF-1	EAI	Cathedral Cove nest	34.01506	119.37112	Prey Remains		Various	17-May-07	J. Pagel	
2	07-MC33-RF-1	SBI	Signal Pt nest	33.47105	119.04166	Prey Remains		Various	9-May-07	B. Latta	

## 2007 Channel Islands Peregrine Falcon Study Final Report

3	07-MC30-RF-1	SCI	Sealion nest	34.07426	119.88335	Prey Remains		Various	11-May-07	B. Latta	
4	07-MC53-RF-1	SCI	Bowen Pt. nest	33.96093	119.72368	Prey Remains		Various	2-Jun-07	J. Pagel	
5	07-MC46-RF-1	SCI	Valley Anchorage nest	33.98623	119.6618	Prey Remains		Various	18-Jun-07	J. Pagel	
6	07-MC38-RF-1	SCI	Blackpoint 03 nest ledge	34.04316	119.88805	Prey remains		Various	14-Aug-07	J. Pagel	Successful nest
7	07-MC19-RF-1	SCI	Laguna nest cliff	33.96037	119.78765	Prey remains		Various	15-Aug-07	J. Pagel	Successful nest
8	07-MC18-RF-1	SCI	Ghirini Knife Edge cliff	34.04633	119.59536	Prey remains		Various	16-Aug-07	J. Pagel	Pre-2007 nest of unknown outcome
9	07-MC47-RF-1	SMI	Crook Pt. nest	34.02349	120.37277	Prey Remains		Various	27-May-07	B. Latta	
10	07-MC28-RF-1	SMI	Bat Rock trad. nest	34.0607	120.35874	Prey Remains		Various	28-May-07	B. Latta	
11	07-MC44-RF-1	SMI	Cardwell Pt. right eyrie	34.02878	120.31123	Prey Remains		Various	29-May-07	B. Latta	
12	07-MC59-RF-1	SMI	Science/Mill-enium nest	34.03308	120.41387	Prey Remains		Various	11-Aug-07	J. Pagel	
13	07-MC17-RF-1	SMI	Hoffman 07 nest	34.04426	120.32501	Prey Remains		Various	12-Aug-07	J. Pagel	Castings
14	07-MC58-RF-1	SMI	Salvador nest	34.07043	120.36257	Prey remains		Various	13-Aug-07	J. Pagel	From nest ledge
15	07-MC58-RF-2	SMI	Salvador nest	34.07043	120.36257	Prey remains		Various	13-Aug-07	J. Pagel	From below nest ledge
16	07-MC55-RF-1	SRI	Soledad nest	34.01207	120.15848	Prey Remains		Various	8-May-07	J. Pagel	
17	07-MC51-RF-1	SRI	Krumholtz nest	33.90104	120.12849	Prey Remains		Various	15-May-07	J. Pagel	
18	07-MC16-RF-1	SRI	Carrington Pt. 07 nest	34.03597	120.05762	Prey Remains		Various	30-May-07	J. Pagel	
19	07-MC34-RF-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Prey Remains		Various	31-May-07	J. Pagel	
20	07-MC27a-RF-1	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	Prey Remains		Various	14-Jun-07	J. Pagel	
21	07-MC50-RF-1	SRI	Trancion nest	33.92627	120.15704	Prey Remains		Various	16-May-07	J. Pagel	

### EGGSHELLS, EGG SHELL FRAGMENTS, AND ADDLED EGGS

No.	Sample ID	Island	Location	Lat	Lon	Type	Band #	Species	Date Collected	Collector	Notes
1	07-MC54-EF-1	EAI	Cathedral Cove nest	34.01506	119.37112	Eggshell Fragments		PEFA	17-May-07	J. Pagel	2007 fragments, Successful nest
2	07-MC33-ES-1	SBI	Signal Pt nest	33.47105	119.04166	Eggshell		PEFA	19-Apr-07	B. Latta	1 of 2 hatched eggs, 3rd egg was pipped and tested alive
3	07-MC33-ES-2	SBI	Signal Pt nest	33.47105	119.04166	Eggshell		PEFA	19-Apr-07	B. Latta	2 of 2 hatched eggs, 3rd egg was pipped and tested alive

## 2007 Channel Islands Peregrine Falcon Study Final Report

4	07-MC33-EF-1	SBI	Signal Pt nest	33.47105	119.04166	Eggshell Fragments		PEFA	9-May-07	B. Latta	2007 fragments, Successful nest
5	07-MC30-EF-1	SCI	Sealion nest	34.07426	119.88335	Eggshell Fragments		PEFA	11-May-07	B. Latta	Successful nest
6	07-MC53-EF-1	SCI	Bowen Pt. nest	33.96093	119.72368	Eggshell Fragments		PEFA	2-Jun-07	J. Pagel	2007 fragments, Successful nest
7	07-MC46-EF-1	SCI	Valley Anchorage nest	33.98623	119.6618	Eggshell Fragments		PEFA	18-Jun-07	J. Pagel	Successful nest
8	07-MC38-EF-1	SCI	Blackpoint 02 nest ledge	34.04472	119.89181	Eggshell Fragments		PEFA	14-Aug-07	J. Pagel	Successful nest
9	07-MC38-EF-2	SCI	Blackpoint 03 nest ledge	34.04316	119.88805	Eggshell Fragments		PEFA	14-Aug-07	J. Pagel	Successful nest
10	07-MC18-EF-1	SCI	Ghirini Knife Edge cliff	34.04633	119.59536	Eggshell Fragments		PEFA	16-Aug-07	J. Pagel	Pre-2007 nest of unknown outcome
11	07-MC47-EF-1	SMI	Crook Pt. nest	34.02349	120.37277	Eggshell Fragments		PEFA	27-May-07	B. Latta	2007 fragments, Successful nest
12	07-MC28-EF-1	SMI	Bat Rock trad. nest	34.0607	120.35874	Eggshell Fragments		PEFA	28-May-07	B. Latta	2007 fragments, Failed nest
13	07-MC28-EF-2	SMI	Bat Rock trad. nest	34.0607	120.35874	Eggshell Fragments		PEFA	28-May-07	B. Latta	older fragments
14	07-MC44-EF-1	SMI	Cardwell Pt. left eyrie	34.02878	120.31123	Eggshell Fragments		PEFA	29-May-07	B. Latta	2007 fragments, Failed nest
15	07-MC44-EF-2	SMI	Cardwell Pt. left eyrie	34.02878	120.31123	Eggshell Fragments		PEFA	29-May-07	B. Latta	older fragments
16	07-MC44-EF-3	SMI	Cardwell Pt. right eyrie	34.02878	120.31123	Eggshell Fragments		PEFA	29-May-07	B. Latta	older fragments, successful nest in 2003
17	07-MC57-AE-1	SMI	Carbon Pt. nest	34.05317	120.38699	Addled Egg		PEFA	9-Jun-07	B. Latta	Failed nest
18	07-MC57-EF-1	SMI	Carbon Pt. nest	34.05317	120.38699	Eggshell Fragments		PEFA	9-Jun-07	B. Latta	2007 fragments, Failed nest
19	07-MC59-EF-1	SMI	Science/Mill- enium nest	34.03308	120.41387	Eggshell Fragments		PEFA	11-Aug-07	J. Pagel	Successful nest
20	07-MC17-EF-1	SMI	Hoffman 07 nest	34.04426	120.32501	Eggshell Fragments		PEFA	12-Aug-07	J. Pagel	Failed nest
21	07-MC17-EF-2	SMI	Hoffman 06 nest ledge #1 scrape	34.04348	120.32495	Eggshell Fragments		PEFA	12-Aug-07	B. Latta	Failed nest (pre-2006 fragments), 1 of 3 scrapes on ledge
22	07-MC17-EF-3	SMI	Hoffman 06 nest ledge #2 scrape	34.04348	120.32495	Eggshell Fragments		PEFA	12-Aug-07	B. Latta	Failed nest(2006 fragments), 1 of 3 scrapes on ledge
23	07-MC17-EF-4	SMI	Hoffman 06 nest ledge #3 scrape	34.04348	120.32495	Eggshell Fragments		PEFA	12-Aug-07	B. Latta	Failed nest(pre-2006 fragments), 1 of 3 scrapes on ledge
24	07-MC17-EF-5	SMI	Hoffman 06 nextdoor nest	34.04348	120.32495	Eggshell Fragments		PEFA	12-Aug-07	B. Latta	Failed nest(pre-2006 fragments), pothole next to 2006 ledge
25	07-MC58-EF-1	SMI	Salvador nest ledge	34.07043	120.36257	Eggshell Fragments		PEFA	13-Aug-07	J. Pagel	Successful nest
26	07-MC55-EF-1	SRI	Soledad nest	34.01207	120.15848	Eggshell Fragments		PEFA	8-May-07	J. Pagel	2007 fragments, Successful nest
27	07-MC51-EF-1	SRI	Krumholtz nest	33.90104	120.12849	Eggshell Fragments		PEFA	15-May-07	J. Pagel	Successful nest
28	07-MC16-EF-1	SRI	Carrington Pt.	34.03597	120.05762	Eggshell		PEFA	30-May-07	J. Pagel	2007 fragments, successful

## 2007 Channel Islands Peregrine Falcon Study Final Report

			07 nest			Fragments					nest
29	07-MC16-EF-2	SRI	Carrington Pt. 06 nest	34.02997	120.06369	Eggshell Fragments		PEFA	31-May-07	B. Latta	2006 fragments, successful nest
30	07-MC34-AE-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Addled Egg		PEFA	31-May-07	J. Pagel	Successful nest
31	07-MC34-ES-1	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Eggshell		PEFA	31-May-07	J. Pagel	1 of 3 hatched eggs
32	07-MC34-ES-2	SRI	Bee R. Cyn Pinnacle 07 nest	33.96681	120.19307	Eggshell		PEFA	31-May-07	J. Pagel	2 of 3 hatched eggs
33	07-MC31-EF-1	SRI	Water Cyn 2006 nest (middle)	33.98094	120.0506	Eggshell Fragments		PEFA	1-Jun-07	J. Pagel	2006 fragments,successful nest
34	07-MC31-EF-2	SRI	Water Cyn 2003 nest (upper)	33.98094	120.0506	Eggshell Fragments		PEFA	1-Jun-07	J. Pagel	2003 fragments, successful nest
35	07-MC31-EF-3	SRI	Water Cyn 200? nest (lower)	33.98094	120.0506	Eggshell Fragments		PEFA	1-Jun-07	J. Pagel	post-2000 fragments, outcome unknown
36	07-MC27a-EF-1	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	Eggshell Fragments		PEFA	14-Jun-07	J.Pagel	2007 fragments, Successful nest
37	07-MC27a-EF-2	SRI	Lobos Cyn. 2007 nest	34.01213	120.09676	Eggshell Fragments		Unk.	14-Jun-07	J.Pagel	Unknown eggshell piece from nest ledge
38	07-MC34-EF-2	SRI	Bee R. Cyn 2006? nest	33.96691	120.19254	Eggshell Fragments		PEFA	14-Jun-07	J. Pagel	Successful nest
39	07-MC50-AE-1	SRI	Trancion nest	33.92627	120.15704	Addled Egg		PEFA	16-May-07	J. Pagel	Successful nest
40	07-MC50-EF-1	SRI	Trancion nest	33.92627	120.15704	Eggshell Fragments		PEFA	16-May-07	J. Pagel	Successful nest
41	07-MC34-AE-2	SRI	Bee R. Cyn 2006? nest	33.96691	120.19254	Addled Egg		PEFA	14-Jun-07	J. Pagel	Successful nest

### EGGSHELLS,EGGSHELL FRAGMENTS, AND ADDLED EGGS COLLECTED BETWEEN 1994-2006

No.	Sample ID	Island	Location	Lat	Lon	Type		Species	Date Collected	Collector	Notes
1	98-MC33-ES-1	SBI	Signal Pt. 97 nest	34.4713	119.04142	Eggshell Fragments		PEFA	24-May-06	B.Latta	2006 and/or earlier fragments, nest was successful some time prior to 2006
2	01-MC38-EF-1	SCI	Blackpoint (Daniel's Ear) nest	34.04472	119.89181	Eggshell Fragments		PEFA	20-Aug-03	B.Latta	2003 fragments, failed 1st clutch
3	98-MC20-ES-1	SCI	West End northwest cove nest	34.07682	119.91843	Eggshell Fragments		PEFA	21-Aug-03	B.Latta	2003 fragment(1), possible failed 2nd clutch

## 2007 Channel Islands Peregrine Falcon Study Final Report

4	99-MC37-ES-1	SMI	Rat Trap 99 nest	34.04851	120.42353	Eggshell		PEFA	21-Jul-01	B.Latta	2001 fragments, successful nest
5	99-MC37-EF-1	SMI	Rat Trap 99 nest	34.04851	120.42353	Eggshell Fragments		PEFA	20-Jun-99	B.Latta	Failed nest
6	98-MC28-ES-1	SMI	Bat Rock traditional nest	34.0607	120.35874	Eggshell Fragments		PEFA	20-Jun-99	B.Latta	Failed nest
7	06-MC36-EF-1	SRI	Lost Hat 2nd nest	33.96162	119.98819	Eggshell Fragments		PEFA	13-Aug-98	B.Latta	1995-1998 fragments, outcome unknown
8	03-MC16-EF-1	SRI	Carrington Pt. 2003 1st clutch nest	34.02934	120.06372	Eggshell Fragments		PEFA	10-Aug-98	B.Latta	1998 fragments, successful nest, 2nd clutch
9	03-MC16-EF-2	SRI	Carrington Pt. 2003 2nd clutch nest	34.03048	120.06278	Eggshell Fragments		PEFA	8-Jul-98	B.Latta	1998 fragments, successful nest
10	98-MC27-ES-2	SRI	Lobos Cyn lower stick nest	34.0118	120.09639	Eggshell Fragments		PEFA	23-Jun-98	B.Latta	1998 fragments, successful nest
11	98-MC34-ES-1	SRI	Bee Rock Cyn pinnacle 98 nest	33.96681	120.19307	Eggshell Fragments		PEFA	17-Jun-98	B.Latta	1997 fragments, failed nest
12	98-MC27-ES-1	SRI	Lobos Cyn upper nest	34.0118	120.09639	Eggshell Fragments		PEFA	12-Jun-98	B.Latta	1998 fragments, 1st clutch, failed nest
13	98-MC37-ES-1	SRI	Lost Hat 98 nest	33.96153	119.98749	Eggshell Fragments		PEFA	11-Jun-98	B.Latta	1998 fragments, successful nest, new territory
14	98-MC31-ES-1	SRI	Water Cyn upper wall 98 nest	33.98074	120.05101	Eggshell Fragments		PEFA	11-Jun-98	B.Latta	1998 fragments, successful nest
15	97-MC27-ES-1	SRI	Lobos Cyn stick upper stick nest	34.0118	120.09639	Eggshell Fragments		PEFA	1-Jun-98	B.Latta	1998 fragments, successful nest
16	97-MC27-ES-2	SRI	Lobos Cyn stick upper stick nest	34.0118	120.09639	Eggshell Fragments		PEFA	4-Sep-97	B.Latta	1997 fragments, successful nest, new pair
17	97-MC34-ES-1	SRI	Bee Rock Cyn pinnacle 97 nest	33.96681	120.19307	Eggshell Fragments		PEFA	4-Sep-97	B.Latta	1997 intact empty egg
18	98-MC21-ES-1	WAI	W. Anacapa Alternate nest	34.01116	119.43767	Eggshell Fragments		PEFA	3-Sep-97	J. Pagel	1997 fragments, successful nest, new territory

**Appendix iii.**

**Protocol for Use of a Digital Egg Monitor for Collecting, Preparing, and Shipping Egg Samples from the 2007 Channel Islands Peregrine Falcon Monitoring Effort**

Joel E. Pagel, Ph.D.  
Carlsbad Fish and Wildlife Office, USFWS  
22 Feb. 2007

All sample collectors should coordinate with Annie Little (USFWS) and Dr. Joel Pagel (USFWS) prior to collection and/or if additional information is required.

*Objectives*

1. Collect presumed dead (addled) or infertile eggs from active nest sites for contaminant analysis.
2. Test accuracy of Digital Egg Monitor (Buddy, Avitronics)
3. Ensure accurate analysis of contaminants in eggs by providing standard methods to transfer egg contents from nest site, to lab, and then into a clean container without introducing contamination.

*Materials*

For field collection: Appropriate University, State and Federal permits; writing utensils; labels; egg collection field container (hard-sided container such as plastic kitchen ware or plastic dry box with foam padding); sheets of chemically-clean<sup>1</sup> aluminum foil, cut to size (approximately 10 x 15 cm), one per egg; digital egg monitor (Buddy), portable peregrine falcon egg incubator, laboratory egg incubator.

For contents removal in laboratory: Data sheets; writing utensils; safety glasses; powder-free latex gloves; laboratory paper wipes such as Kimwipes®; distilled, deionized (DD) water or equivalently pure water; clean sponge; balance (to 0.01 g); vernier calipers (to 0.01 mm); immersion chamber with beaker and wire loops; Teflon® bags, one per egg; chemically-clean stainless steel serrated blades (such as high-quality steak knives); chemically-clean stainless steel scalpel blades (No. 21 or No. 22 with No. 4 handles or similar size); chemically-clean aluminum foil sheets (approximately 30 x 30 cm square), 1 per egg; ball-tip micrometer (to 0.01 mm).

<sup>1</sup>Chemically-clean aluminum foil has been rinsed with reagent-grade acetone and hexanes on the dull side and allowed to air-dry; dull side is then considered the “clean” side. Chemically-clean stainless instruments are rinsed with 10-20 % nitric acid, then doubly-distilled or equivalently purified water, air-dried, then rinsed with reagent-grade acetone and hexanes and air-dried.

*Procedures*

No more than four active peregrine falcon nests will be entered in the safest possible way to protect biologists, peregrine falcons, and nearby nesting seabirds. These nest sites will include one site on Catalina Island and one site on Santa Barbara Island that have traditionally failed. The other two sites will be nesting locations where previous contaminant data was collected in 1992-1993 from addled eggs. Entry to collect eggs will occur 7-14 days after hard incubation commences, or if nest sites are abandoned during onset of incubation. If all eggs are collected from a nest site, the adult peregrines may recycle. Egg collection will not occur a second time at a nest; the second clutch will be allowed to succeed or fail without human intervention. Nests may be entered a second time to collect eggshell fragments or band young if practicable. If nest sites fail, entry to the nest ledge will be encouraged to collect any addled eggs that may have been abandoned, or eggshell fragments.

*At the nest site-on the ledge:*

Embryonic heartbeat will be detected in whole, cracked, or pitted eggs using a digital egg monitor placed on a flat surface within the nest ledge. Eggs will be handled using sterile rubber gloves. If an embryonic heartbeat is detected using the digital egg monitor on any whole, cracked or pitted egg, (at any heartbeat/minute rate), the egg will be left on the nest ledge within the nest scrape and allowed to be re-incubated by the adult peregrines to hatch or failure.

If no embryonic heartbeat is detected in whole eggs, the egg will be placed in the field container (described above). If a pitted or cracked egg is found in the nest, and it has no embryonic heartbeat, chemically clean aluminum foil (dull side next to egg) will be placed on the foam egg cutout in the field container.

Field data collected will be standardized and will include nest name, number, coordinates (DD.DDD), egg description and identifying number, and presence of adults. Eggshell fragments in the nest scrape from broken eggs will be collected properly labeled.

*At the portable incubator:*

When eggs are transferred to the portable incubator, whole eggs will be treated as live eggs and will be placed in the egg tray of the pre-heated portable incubator. Eggs that are pitted or cracked will be placed on a piece of chemically clean aluminum foil that will be placed in the egg tray.

Eggs will be transported in the portable incubator from the field to Bill Murphy's facilities at the Santa Cruz Predatory Bird Research Group, U.C. Santa Cruz, Santa Cruz, CA.

*At the laboratory incubator:*

Whole, cracked and pitted eggs will be candled to ascertain developmental stage of the embryo, or to determine if an embryo is present. All eggs will be incubated to full term,

based on field knowledge of nesting chronology if the egg cannot be accurately candled. Cracked or pitted eggs will not be repaired using standard methods (Elmer's glue), however will be kept in high humidity incubator if available. Eggs will be treated as live eggs until the end of presumed incubation period or until USFWS recommends cessation of incubation.

At the end of the incubation period, eggs will be candled, and tested with a digital egg monitor. If confirmed dead, contents of eggs will be removed and used for contaminant analysis. If any eggs hatch, chicks will be raised using standard methods to 14-16 days of age. Chicks will be transferred and fostered into a wild nest site with a comparable nesting chronology either a) on the Channel Islands (preferred), b) in California, or c) Oregon.

Confirmed addled eggs that have been incubated to full term will be wrapped one each in clean aluminum foil (dull side next to the egg). The foil should act as a second skin, which keeps the eggshell together and the contents inside should the egg be cracked in transit. Place the wrapped egg inside I-chem jars, then to refrigeration for eventual transferal to the Carlsbad USFWS office.

*Preparation of eggs for contaminant analysis:*

The USFWS protocol from the National Monitoring Plan as detailed below will be used for laboratory preparation of the addled egg for contaminant analysis (see USFWS 2003, Monitoring Plan for the American Peregrine Falcon; Appendix G. USFWS, Div. End. Species and Migratory Birds and State Programs, Pacific Region, Portland, OR).

In the laboratory, use one data form per egg. Wear powder-free latex gloves and safety glasses (severe eye infection can result from contact with rotting egg contents). Carefully check for cracks in shell; if present, do not wet or immerse the egg; this can be most effectively done using the candler; hairline cracks can be difficult to impossible to see. Holding the candler light parallel to the shell may reveal unseen cracks by the slightly raised portion showing the underlying white of the shell). If debris is present, rinse egg in DD water while gently scrubbing with sponge. Dry the egg. Record the mass (g) of the whole egg, then measure the length and breadth of the egg at their greatest dimensions with calipers (caliper jaws parallel to the longitudinal axis of the egg for length, perpendicular to the longitudinal axis of the egg for breadth). Compute average of three measurements for final width and length measurements.

Measure total egg volume by water displacement. Fill the immersion chamber with distilled water past the point where water comes out of the spigot. Let drain until water stops coming out of the spigot. Place a clean beaker on a balance, zero the balance, and place the balance and beaker under the spigot. Immerse egg with wire loops until top of egg is just under the water surface. Hold the egg steady until water stops draining out of spigot into the beaker. The readout on the balance will reflect only the weight of water that has gone into the beaker, if you zeroed the balance after the beaker was placed on it. The weight of water is the approximate egg volume, assuming that egg density is similar



to water (1gm = 1 ml). For example, 40 gm displaced water = 40 ml of water, and 40 ml egg volume. Dry the egg.

While transferring egg contents to Teflon® bag, avoid letting contents run over your hands into the bag. Note that addled eggs can be full of decomposition products, producing gaseous explosions at any weak point in the shell, including the score or where membranes are first exposed. Working with a refrigerated, cool egg reduces this potential, but be prepared for egg explosions – and wear safety glasses.

Create a catch basin out of the aluminum foil (chemically-clean side up) by turning edges up and securing the corners. This will catch egg contents in case they spill over the edge of the bag. Use a separate piece of foil for each sample. The foil also is a clean place to place your instruments when they are not in use. Tare balance with Teflon® bag, then place bag in center of aluminum foil.

Score egg at the equator with a clean serrated blade or scalpel. Cradle the egg in one hand without squeezing too tightly, and gently score while rotating the egg. Many light strokes are preferable to a fewer deeper strokes, increasing the evenness of the score and decreasing the possibility of fractured eggshells. Continue to score until you see the membrane, which usually appears gray underneath the white of the eggshell. Try to expose the membrane evenly around the entire egg.

Place the egg over the open bag and cut through membranes with the scalpel. Pour contents into bag, and use the scalpel to gently scrape if necessary. Close the bag. Note where the membranes are, as this is important for thickness measurements. For fresh eggs, both membranes often stay with the shell, but as the embryo develops the inner membrane tends to stick with the embryo. If you cannot determine where the membranes are, it often becomes clearer after the eggshell and membranes have dried. Record mass of full bag, then subtract tare mass to compute egg contents mass. Label the bag with nest and egg identification information. Freeze the sample (-40° C is preferable but 0° C is adequate) until shipment to central repository.

If egg is developed, estimate age of embryo. Peregrine incubation is 29-33 days; estimate age of embryo to first, second, third, or fourth quarter. Photographic records of avian embryo development provide reference points to make this determination. Note amount of decay (no decay, slightly decayed, or rotten) and examine for deformities, particularly bill deformities such as crossed bills or lack of jaws, but also lack of skull bones, club feet, rotated ankles, or dwarfed appendages.

Rinse the eggshell halves with cool water and allow to air dry. Using an ultra-fine tip marker or pencil, identify each shell half (with nest and egg information). Dry eggshells at room temperature for 10-30 days, or until they have attained a constant mass. Then, measure thickness at three points near the equator on each shell half using ball-tip micrometer. Note whether you measured the membranes, as museum specimen thickness measurements often include the membranes. Finally, record the mass of the dried eggshell (to 0.001 g). This information is also used to compare to museum specimens.

## 2007 Channel Islands Peregrine Falcon Study Final Report

Compute conversion factor, as explained on the data sheet. Historically, contaminant concentrations were multiplied by this conversion factor to get volume-adjusted residue data.

### *Shipping*

Place frozen, bagged contents in a cooler with dry ice (know the labeling requirements of your shipping company for dry ice) for shipping. If you are unable to find dry ice, contact Jerry Zschau (information below) for shipping instructions. Send via overnight service to the central storage repository:

#### Woods Hole Oceanographic Institute

Alpha Woods Hole Laboratory  
Attention: Jerry Zschau  
375 Paramount Drive  
Suite 2  
Raynham, MA 02767

[gzschau@alphalab.com](mailto:gzschau@alphalab.com)

Notify the recipient by e-mail prior to shipping, and try to ship on Monday, Tuesday, or Wednesday to avoid weekend delays.

# 2007 Channel Islands Peregrine Falcon Study Final Report

## Appendix iv. History of Peregrine Falcon Recovery on the Channel Islands, 1986-2007

Island	Territory	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
SMI	Hoffman Pt.	T	A?	F	M	I	A	M	F	F	F	I+	A	A	O	ND	ND	ND	A	A	ND	F	F
	Bat Rock							M	F	2	A	I+	I+	1	2	I+	ND	ND	A	3	ND	F	F
	Rat Trap														F	F	ND	ND	A	ND	ND	T	I
	Cardwell																		I+	A	ND	A	F
	Crooked																			A	A	2+	3
	Carbon Pt.																					F	F
	Sci. Pt./Mill.																					W/O?	1
	Salvador Pt.																			3?	ND	A	3
SRI	Carrington Pt.				O?	O	O	T	I	1	2	1	2	2	ND	3	ND	ND	F?	O?			2
	Lime Pt.							A	F	I	I	A	2	2	ND	3	ND	ND	3	O?	ND	T	3
	Water Cyn.										3	3	4	2	ND	2	ND	2	2	A	ND	2	T
	Bee R. Cyn											A	1	3	ND	O?	ND	ND	ND	I+	ND	A	2
	Jaw Gulch											O	F	1	ND	ND	ND	ND	ND	ND	ND	ND	I
	Lost Hat													2	ND	U	ND	ND	O	ND	ND	F	O
	Trancion																					2	2
	Krumholtz																			A?		2	3
	Gnoma																			A?			F
	Soledad																						2
SCI	Gherini			UC	UC	UC	T	4(2nd)	3	2	A	2+	A	ND	ND	ND	2	ND	A	ND	ND	F	F
	West End				M	2	A	2(2nd)	3	1	3	3	A	A	ND	ND	ND	ND	ND	ND	ND	ND	I
	Laguna						O	M	I+	T	1	I?	A	ND	ND	ND	ND	A	ND	ND	O?	I+	
	Sea Lion								3	F	ND	T	2	ND	ND	ND	ND	3	ND	O?	ND	A	3
	Black Pt.															A	1	3	2	ND	ND	A	F
	Arch Rock																		I+	ND	ND	ND	2
	Valley Anch.																				UC	A	1
	Cavern Pt.																					A	T
	Bowen Pt.																						2
	Diablo Pt.																						O?
	Little Scorpion																						UC
Ana	West Ana.				3	3	2	3(2nd)	2	2	F?	F?	F	1	ND	ND	ND	2	A?	ND	ND	ND	A
	Middle A.																		1	ND	ND	ND	ND
	East A.																						1
SBI	Santa Barbara										T	A	A	A	A	ND	ND	A	I+?	ND	ND	ND	3

## 2007 Channel Islands Peregrine Falcon Study Final Report

SCA	Long Pt.																		A	A	ND	I	W/I
	Bullethead																			F	ND	O?	W/I
SCL	China Pt.																						UC
SNI	Southwest																						W/I
	Southeast																						O

A = Active - contained a resident pair throughout the breeding season and a breeding attempt was documented.

T = Transitional - contained a new or immature pair member and no breeding attempt was observed.

O = Occupied - contained one resident falcon throughout the breeding season.

F = Failed – eggs were laid but failed to hatch.

1, 2, etc. = number of young produced.

1+ = more than one young was produced but total number was undetermined.

M = Manipulated – SCPBRG removed eggs and fostered captive-hatched young into the nest

I = Inactive - was known to have been active at least once from 1984 to the present, but was vacant during the 2007 breeding season.

W = Wintering - contained one or more transient peregrines that left by mid-April.

UC = Unconfirmed - unsubstantiated reports from non-SCPBRG personnel of a pair or single peregrine residing at a cliff throughout the breeding season.

ND = Not Determined – territory was either not surveyed or there was insufficient observation to determine status

## 2007 Channel Islands Peregrine Falcon Study Final Report

Appendix v. Complete list of measurements of all egg, eggshell, and eggshell fragment samples collected on the Channel Islands from 1999-2000.

SAMPLE	TYPE	SITE	YEAR	THICKNESS	W/MEMBRANE	THINNING
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.201	0.264	27.47
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.191	0.254	30.22
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.189	0.252	30.77
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.189	0.252	30.77
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.200	0.263	27.75
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.191	0.254	30.22
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.198	0.261	28.30
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.193	0.256	29.67
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.198	0.261	28.30
99-MC37-EF-1	fragment	SMI Rat Trap	1999	0.203	0.266	26.92
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.230	0.293	19.51
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.237	0.300	17.58
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.221	0.284	21.98
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.229	0.292	19.78
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.232	0.295	18.96
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.220	0.283	22.25
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.234	0.297	18.41
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.222	0.285	21.70
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.233	0.296	18.68
99-MC37-ES-1	eggshell	SMI Rat Trap	1999	0.229	0.292	19.78
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.291	20.05
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.290	20.33
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.289	20.60
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.287	21.15
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.288	20.88
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.290	20.33
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.289	20.60
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.289	20.60
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.288	20.88
99-MC37-ES-1	eggshell	SMI Rat Trap	1999		0.288	20.88
01-MC38-EF-1	fragment	SCI Black Point	2001	0.237	0.300	17.58
01-MC38-EF-1	fragment	SCI Black Point	2001	0.242	0.305	16.21
01-MC38-EF-1	fragment	SCI Black Point	2001	0.255	0.318	12.64
01-MC38-EF-1	fragment	SCI Black Point	2001	0.242	0.305	16.21
01-MC38-EF-1	fragment	SCI Black Point	2001	0.248	0.311	14.56
01-MC38-EF-1	fragment	SCI Black Point	2001	0.230	0.293	19.51
01-MC38-EF-1	fragment	SCI Black Point	2001	0.217	0.280	23.08
01-MC38-EF-1	fragment	SCI Black Point	2001	0.231	0.294	19.23
01-MC38-EF-1	fragment	SCI Black Point	2001	0.239	0.302	17.03
01-MC38-EF-1	fragment	SCI Black Point	2001	0.242	0.305	16.21
07-MC38-EF-1	fragment	SCI Black Point	2002	0.244	0.307	15.66
07-MC38-EF-1	fragment	SCI Black Point	2002	0.208	0.271	25.55
07-MC38-EF-1	fragment	SCI Black Point	2002	0.260	0.323	11.26
07-MC38-EF-1	fragment	SCI Black Point	2002	0.243	0.306	15.93

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC38-EF-1	fragment	SCI Black Point	2002	0.210	0.273	25.00
07-MC38-EF-1	fragment	SCI Black Point	2002	0.219	0.282	22.53
07-MC38-EF-1	fragment	SCI Black Point	2002	0.261	0.324	10.99
07-MC38-EF-1	fragment	SCI Black Point	2002	0.229	0.292	19.78
07-MC38-EF-1	fragment	SCI Black Point	2002	0.249	0.312	14.29
07-MC38-EF-1	fragment	SCI Black Point	2002	0.241	0.304	16.48
03-MC16-EF-1	fragment	SRI Carrington	2003	0.270	0.333	8.52
03-MC16-EF-1	fragment	SRI Carrington	2003	0.267	0.330	9.34
03-MC16-EF-1	fragment	SRI Carrington	2003	0.281	0.344	5.49
03-MC16-EF-1	fragment	SRI Carrington	2003	0.248	0.311	14.56
03-MC16-EF-1	fragment	SRI Carrington	2003	0.202	0.265	27.20
03-MC16-EF-1	fragment	SRI Carrington	2003	0.230	0.293	19.51
03-MC16-EF-1	fragment	SRI Carrington	2003	0.251	0.314	13.74
03-MC16-EF-1	fragment	SRI Carrington	2003	0.250	0.313	14.01
03-MC16-EF-1	fragment	SRI Carrington	2003	0.270	0.333	8.52
03-MC16-EF-1	fragment	SRI Carrington	2003	0.272	0.335	7.97
03-MC16-EF-2	fragment	SRI Carrington	2003	0.180	0.243	33.24
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.263	0.274	24.73
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.230	0.293	19.51
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.211	0.274	24.73
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.267	0.330	9.34
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.245	0.308	15.38
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.190	0.253	30.49
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.198	0.261	28.30
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.242	0.305	16.21
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.246	0.309	15.11
07-MC31-EF-2	fragment	SRI Water Canyon	2003	0.262	0.325	10.71
07-MC38-EF-2	fragment	SCI Black Point	2003	0.233	0.296	18.68
07-MC38-EF-2	fragment	SCI Black Point	2003	0.212	0.275	24.45
07-MC38-EF-2	fragment	SCI Black Point	2003	0.214	0.277	23.90
07-MC38-EF-2	fragment	SCI Black Point	2003	0.215	0.278	23.63
07-MC38-EF-2	fragment	SCI Black Point	2003	0.220	0.283	22.25
07-MC38-EF-2	fragment	SCI Black Point	2003	0.247	0.310	14.84
07-MC38-EF-2	fragment	SCI Black Point	2003	0.227	0.290	20.33
07-MC38-EF-2	fragment	SCI Black Point	2003	0.240	0.303	16.76
07-MC38-EF-2	fragment	SCI Black Point	2003	0.231	0.294	19.23
07-MC38-EF-2	fragment	SCI Black Point	2003	0.208	0.271	25.55
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.199	0.262	28.02
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.178	0.241	33.79
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.188	0.251	31.04
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.201	0.264	27.47
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.202	0.265	27.20
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.200	0.263	27.75
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.189	0.252	30.77
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.191	0.254	30.22
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.200	0.263	27.75
07-MC44-EF-3	fragment	SMI Cardwell Point	2003	0.201	0.264	27.47
07-MC16-EF-2	fragment	SRI Carrington	2006	0.245	0.308	15.38

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC16-EF-2	fragment	SRI Carrington	2006	0.237	0.300	17.58
07-MC16-EF-2	fragment	SRI Carrington	2006	0.248	0.311	14.56
07-MC16-EF-2	fragment	SRI Carrington	2006	0.226	0.289	20.60
07-MC16-EF-2	fragment	SRI Carrington	2006	0.224	0.287	21.15
07-MC16-EF-2	fragment	SRI Carrington	2006	0.240	0.303	16.76
07-MC16-EF-2	fragment	SRI Carrington	2006	0.237	0.300	17.58
07-MC16-EF-2	fragment	SRI Carrington	2006	0.250	0.313	14.01
07-MC16-EF-2	fragment	SRI Carrington	2006	0.239	0.302	17.03
07-MC16-EF-2	fragment	SRI Carrington	2006	0.230	0.293	19.51
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.225	0.288	20.88
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.211	0.274	24.73
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.229	0.292	19.78
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.209	0.272	25.27
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.211	0.274	24.73
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.210	0.273	25.00
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.226	0.289	20.60
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.224	0.287	21.15
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.218	0.281	22.80
07-MC17-EF-3	fragment	SMI Hoffman Point	2006	0.203	0.266	26.92
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.236	0.299	17.86
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.287	0.350	3.85
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.270	0.333	8.52
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.239	0.302	17.03
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.233	0.296	18.68
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.257	0.320	12.09
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.263	0.326	10.44
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.259	0.322	11.54
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.260	0.323	11.26
07-MC31-EF-1	fragment	SRI Water Canyon	2006	0.239	0.302	17.03
07-MC16-EF-1	fragment	SRI Carrington	2007	0.283	0.346	4.95
07-MC16-EF-1	fragment	SRI Carrington	2007	0.275	0.338	7.14
07-MC16-EF-1	fragment	SRI Carrington	2007	0.238	0.301	17.31
07-MC16-EF-1	fragment	SRI Carrington	2007	0.259	0.322	11.54
07-MC16-EF-1	fragment	SRI Carrington	2007	0.280	0.343	5.77
07-MC16-EF-1	fragment	SRI Carrington	2007	0.248	0.311	14.56
07-MC16-EF-1	fragment	SRI Carrington	2007	0.277	0.340	6.59
07-MC16-EF-1	fragment	SRI Carrington	2007	0.260	0.323	11.26
07-MC16-EF-1	fragment	SRI Carrington	2007	0.241	0.304	16.48
07-MC16-EF-1	fragment	SRI Carrington	2007	0.256	0.319	12.36
07-MC16-EF-1	fragment	SRI Carrington	2007		0.318	12.64
07-MC16-EF-1	fragment	SRI Carrington	2007		0.300	17.58
07-MC16-EF-1	fragment	SRI Carrington	2007		0.330	9.34
07-MC16-EF-1	fragment	SRI Carrington	2007		0.320	12.09
07-MC16-EF-1	fragment	SRI Carrington	2007		0.313	14.01
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.260	0.323	11.26
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.250	0.313	14.01
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.256	0.319	12.36
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.231	0.294	19.23

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC17-EF-1	fragment	SMI Hoffman	2007	0.235	0.298	18.13
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.279	0.342	6.04
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.220	0.283	22.25
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.256	0.319	12.36
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.250	0.313	14.01
07-MC17-EF-1	fragment	SMI Hoffman	2007	0.255	0.318	12.64
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.245	0.308	15.38
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.231	0.294	19.23
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.230	0.293	19.51
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.241	0.304	16.48
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.244	0.307	15.66
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.240	0.303	16.76
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.238	0.301	17.31
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.240	0.303	16.76
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.231	0.294	19.23
07-MC27a-EF-1	fragment	SRI Lobos Canyon	2007	0.237	0.300	17.58
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.240	0.303	16.76
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.199	0.262	28.02
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.235	0.298	18.13
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.222	0.285	21.70
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.220	0.283	22.25
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.229	0.292	19.78
07-MC28-EF-1	fragment	SMI Bat Rock	2007	0.226	0.289	20.60
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.234	0.297	18.41
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.228	0.291	20.05
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.232	0.295	18.96
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.241	0.304	16.48
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.244	0.307	15.66
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.252	0.315	13.46
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.232	0.295	18.96
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.258	0.321	11.81
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.245	0.308	15.38
07-MC30-EF-1	fragment	SCI Sea Lion	2007	0.229	0.292	19.78
07-MC30-EF-1	fragment	SCI Sea Lion	2007		0.301	17.31
07-MC30-EF-1	fragment	SCI Sea Lion	2007		0.306	15.93
07-MC30-EF-1	fragment	SCI Sea Lion	2007		0.300	17.58
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.222	0.285	21.70
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.231	0.294	19.23
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.221	0.284	21.98
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.229	0.292	19.78
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.224	0.287	21.15
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.229	0.292	19.78
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.230	0.293	19.51
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.230	0.293	19.51



## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.231	0.294	19.23
07-MC33-EF-1	fragment	Santa Barbara Island	2007	0.220	0.283	22.25
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.210	0.273	25.00
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.229	0.292	19.78
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.221	0.284	21.98
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.217	0.280	23.08
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.222	0.285	21.70
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.223	0.286	21.43
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.220	0.283	22.25
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.217	0.280	23.08
07-MC33-ES-1	eggshell	Santa Barbara Island	2007	0.221	0.284	21.98
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.261	28.30
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.251	31.04
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.250	31.32
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.260	28.57
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.248	31.87
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.262	28.02
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.250	31.32
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.266	26.92
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.265	27.20
07-MC33-ES-1	eggshell	Santa Barbara Island	2007		0.261	28.30
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.223	0.286	21.43
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.226	0.289	20.60
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.223	0.286	21.43
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.221	0.284	21.98
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.224	0.287	21.15
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.227	0.290	20.33
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.228	0.291	20.05
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.227	0.290	20.33
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.233	0.296	18.68
07-MC33-ES-2	eggshell	Santa Barbara Island	2007	0.223	0.286	21.43
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.307	15.66
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.308	15.38
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.295	18.96
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.304	16.48
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.299	17.86
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.303	16.76
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.299	17.86
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.301	17.31
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.308	15.38
07-MC34-AE-1	addled egg	SRI Bee Rock Canyon	2007		0.310	14.84
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.274	0.337	7.42
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.285	0.348	4.40

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.284	0.347	4.67
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.277	0.347	4.67
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.284	0.335	7.97
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.272	0.344	5.49
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.281	0.333	8.52
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.270	0.334	8.24
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.271	0.344	5.49
07-MC34-ES-1	eggshell	SRI Bee Rock Canyon	2007	0.281	0.344	5.49
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.261	0.324	10.99
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.270	0.333	8.52
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.270	0.333	8.52
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.272	0.335	7.97
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.265	0.328	9.89
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.265	0.328	9.89
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.270	0.333	8.52
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.269	0.332	8.79
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.261	0.324	10.99
07-MC34-ES-2	eggshell	SRI Bee Rock Canyon	2007	0.259	0.322	11.54
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.201	0.264	27.47
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.288	0.351	3.57
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.215	0.278	23.63
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.210	0.273	25.00
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.291	0.354	2.75
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.284	0.347	4.67
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.321	0.384	-5.49
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.200	0.263	27.75
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.195	0.258	29.12
07-MC44-EF-1	fragment	SMI Cardwell Point	2007	0.341	0.404	-10.99
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.212	0.275	24.45
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.191	0.254	30.22
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.196	0.259	28.85
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.199	0.262	28.02
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.200	0.263	27.75
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.193	0.256	29.67
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.213	0.276	24.18
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.214	0.277	23.90
07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.208	0.271	25.55

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC46-EF-1	fragment	SCI Valley Anchorage	2007	0.213	0.276	24.18
07-MC47-EF-1	fragment	SMI Crooked	2007	0.253	0.316	13.19
07-MC47-EF-1	fragment	SMI Crooked	2007	0.257	0.320	12.09
07-MC47-EF-1	fragment	SMI Crooked	2007	0.268	0.331	9.07
07-MC47-EF-1	fragment	SMI Crooked	2007	0.250	0.313	14.01
07-MC47-EF-1	fragment	SMI Crooked	2007	0.266	0.329	9.62
07-MC47-EF-1	fragment	SMI Crooked	2007	0.262	0.325	10.71
07-MC47-EF-1	fragment	SMI Crooked	2007	0.217	0.280	23.08
07-MC47-EF-1	fragment	SMI Crooked	2007	0.253	0.316	13.19
07-MC47-EF-1	fragment	SMI Crooked	2007	0.262	0.325	10.71
07-MC47-EF-1	fragment	SMI Crooked	2007	0.259	0.322	11.54
07-MC47-EF-1	fragment	SMI Crooked	2007		0.318	12.64
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.359	1.37
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.358	1.65
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.353	3.02
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.360	1.10
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.357	1.92
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.357	1.92
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.360	1.10
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.362	0.55
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.359	1.37
07-MC50-AE-1	addled egg	SRI Trancion	2007		0.360	1.10
07-MC50-EF-1	fragment	SRI Trancion	2007	0.239	0.302	17.03
07-MC50-EF-1	fragment	SRI Trancion	2007	0.228	0.291	20.05
07-MC50-EF-1	fragment	SRI Trancion	2007	0.232	0.295	18.96
07-MC50-EF-1	fragment	SRI Trancion	2007	0.237	0.300	17.58
07-MC50-EF-1	fragment	SRI Trancion	2007	0.277	0.340	6.59
07-MC50-EF-1	fragment	SRI Trancion	2007	0.286	0.349	4.12
07-MC50-EF-1	fragment	SRI Trancion	2007	0.264	0.327	10.16
07-MC50-EF-1	fragment	SRI Trancion	2007	0.229	0.292	19.78
07-MC50-EF-1	fragment	SRI Trancion	2007	0.271	0.334	8.24
07-MC50-EF-1	fragment	SRI Trancion	2007	0.236	0.299	17.86
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.252	0.301	17.31
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.255	0.306	15.93
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.207	0.300	17.58
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.241	0.304	16.48
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.219	0.282	22.53
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.219	0.282	22.53
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.257	0.320	12.09
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.199	0.262	28.02
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.211	0.274	24.73
07-MC51-EF-1	fragment	SRI Krumhotz	2007	0.248	0.311	14.56
07-MC51-EF-1	fragment	SRI Krumhotz	2007		0.318	12.64
07-MC51-EF-1	fragment	SRI Krumhotz	2007		0.314	13.74

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC51-EF-1	fragment	SRI Krumhotz	2007		0.320	12.09
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.201	0.264	27.47
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.206	0.269	26.10
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.231	0.294	19.23
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.192	0.255	29.95
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.240	0.303	16.76
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.197	0.260	28.57
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.203	0.266	26.92
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.238	0.301	17.31
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.232	0.295	18.96
07-MC53-EF-1	fragment	SCI Bowen Point	2007	0.230	0.293	19.51
07-MC53-EF-1	fragment	SCI Bowen Point	2007		0.312	14.29
07-MC54-EF-1	fragment	East Anacapa	2007	0.235	0.298	18.13
07-MC54-EF-1	fragment	East Anacapa	2007	0.219	0.282	22.53
07-MC54-EF-1	fragment	East Anacapa	2007	0.234	0.297	18.41
07-MC54-EF-1	fragment	East Anacapa	2007	0.232	0.295	18.96
07-MC54-EF-1	fragment	East Anacapa	2007	0.219	0.282	22.53
07-MC54-EF-1	fragment	East Anacapa	2007	0.241	0.304	16.48
07-MC54-EF-1	fragment	East Anacapa	2007	0.246	0.309	15.11
07-MC54-EF-1	fragment	East Anacapa	2007	0.230	0.293	19.51
07-MC54-EF-1	fragment	East Anacapa	2007	0.230	0.293	19.51
07-MC54-EF-1	fragment	East Anacapa	2007	0.234	0.297	18.41
07-MC54-EF-1	fragment	East Anacapa	2007		0.318	12.64
07-MC55-EF-1	fragment	SRI Soledad	2007	0.227	0.290	20.33
07-MC55-EF-1	fragment	SRI Soledad	2007	0.230	0.293	19.51
07-MC55-EF-1	fragment	SRI Soledad	2007	0.250	0.313	14.01
07-MC55-EF-1	fragment	SRI Soledad	2007	0.248	0.311	14.56
07-MC55-EF-1	fragment	SRI Soledad	2007	0.237	0.300	17.58
07-MC55-EF-1	fragment	SRI Soledad	2007	0.231	0.294	19.23
07-MC55-EF-1	fragment	SRI Soledad	2007	0.232	0.295	18.96
07-MC55-EF-1	fragment	SRI Soledad	2007	0.251	0.314	13.74
07-MC55-EF-1	fragment	SRI Soledad	2007	0.254	0.317	12.91
07-MC55-EF-1	fragment	SRI Soledad	2007	0.251	0.314	13.74
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.197	0.279	23.35
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.210	0.280	23.08
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.177	0.279	23.35
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.181	0.282	22.53
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.211	0.283	22.25
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.210	0.281	22.80
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.178	0.282	22.53
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.182	0.290	20.33
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.216	0.287	21.15
07-MC57-AE-1	addled egg	SMI Carbon Point	2007	0.210	0.278	23.63
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.183	0.246	32.42

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.187	0.250	31.32
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.219	0.282	22.53
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.200	0.263	27.75
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.206	0.269	26.10
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.205	0.268	26.37
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.204	0.267	26.65
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.199	0.262	28.02
07-MC57-EF-1	fragment	SMI Carbon Point	2007	0.207	0.270	25.82
07-MC58-EF-1	fragment	SMI Salvador	2007	0.209	0.272	25.27
07-MC58-EF-1	fragment	SMI Salvador	2007	0.209	0.272	25.27
07-MC58-EF-1	fragment	SMI Salvador	2007	0.241	0.304	16.48
07-MC58-EF-1	fragment	SMI Salvador	2007	0.200	0.263	27.75
07-MC58-EF-1	fragment	SMI Salvador	2007	0.202	0.265	27.20
07-MC58-EF-1	fragment	SMI Salvador	2007	0.270	0.333	8.52
07-MC58-EF-1	fragment	SMI Salvador	2007	0.270	0.333	8.52
07-MC58-EF-1	fragment	SMI Salvador	2007	0.201	0.264	27.47
07-MC58-EF-1	fragment	SMI Salvador	2007	0.280	0.343	5.77
07-MC58-EF-1	fragment	SMI Salvador	2007	0.199	0.262	28.02
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.188	0.251	31.04
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.207	0.270	25.82
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.198	0.261	28.30
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.180	0.243	33.24
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.192	0.255	29.95
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.224	0.287	21.15
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.200	0.263	27.75
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.196	0.259	28.85
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.191	0.254	30.22
07-MC59-EF-1	fragment	SMI Science/Millennium	2007	0.191	0.254	30.22
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.231	0.294	19.23
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.231	0.294	19.23
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.220	0.283	22.25
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.223	0.286	21.43
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.209	0.272	25.27
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.210	0.273	25.00
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.213	0.276	24.18
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.236	0.299	17.86
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.237	0.300	17.58
07-MC17-EF-4	fragment	SMI Hoffman Point	< 2006	0.239	0.302	17.03
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.237	0.300	17.58
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.225	0.288	20.88
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.232	0.295	18.96
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.285	0.348	4.40
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.251	0.314	13.74
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.259	0.322	11.54

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.210	0.273	25.00
07-MC17-EF-2	fragment	SMI Hoffman Point	<2006	0.227	0.290	20.33
07-MC17-EF-5	fragment	SMI Hoffman Point	<2006	0.239	0.302	17.03
07-MC17-EF-5	fragment	SMI Hoffman Point	<2006	0.215	0.278	23.63
07-MC17-EF-5	fragment	SMI Hoffman Point	<2006	0.209	0.272	25.27
07-MC17-EF-5	fragment	SMI Hoffman Point	<2006	0.240	0.303	16.76
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.250	0.313	14.01
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.268	0.331	9.07
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.244	0.307	15.66
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.260	0.323	11.26
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.251	0.314	13.74
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.200	0.263	27.75
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.239	0.302	17.03
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.237	0.300	17.58
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.229	0.292	19.78
07-MC28-EF-2	fragment	SMI Bat Rock	<2007	0.256	0.319	12.36
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.201	0.314	13.74
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.197	0.317	12.91
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.202	0.300	17.58
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.200	0.311	14.56
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.194	0.319	12.36
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.219	0.320	12.09
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.200	0.302	17.03
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.223	0.319	12.36
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.214	0.311	14.56
07-MC34-AE-2	addled egg	SRI Bee Rock Canyon	<2007	0.210	0.316	13.19
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.300	0.363	0.27
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.307	0.370	-1.65
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.296	0.359	1.37
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.300	0.363	0.27
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.305	0.368	-1.10
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.297	0.360	1.10
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.298	0.361	0.82
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.288	0.351	3.57
07-MC34-EF-2	fragment	SRI Bee Rock Canyon	<2007	0.303	0.366	-0.55
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.309	0.372	-2.20
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.269	0.332	8.79
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.320	0.383	-5.22
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.315	0.378	-3.85

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.290	0.353	3.02
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.289	0.352	3.30
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.311	0.374	-2.75
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.307	0.370	-1.65
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.302	0.365	-0.27
07-MC44-EF-2	fragment	SMI Cardwell Point	<2007	0.350	0.413	-13.46
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.271	0.334	8.24
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.278	0.341	6.32
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.269	0.332	8.79
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.280	0.343	5.77
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.257	0.320	12.09
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.272	0.335	7.97
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.271	0.334	8.24
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.275	0.338	7.14
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.271	0.334	8.24
07-MC31-EF-3	fragment	SRI Water Canyon	2000-2002	0.270	0.333	8.52
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.187	0.250	31.32
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.290	0.353	3.02
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.288	0.351	3.57
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.279	0.342	6.04
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.280	0.343	5.77
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.280	0.343	5.77
07-MC18-EF-1	fragment	SCI Gherini	2006?	0.276	0.339	6.87
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.273	0.336	7.69
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.220	0.283	22.25
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.239	0.302	17.03
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.210	0.273	25.00
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.309	0.372	-2.20
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.292	0.355	2.47
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.233	0.296	18.68
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.220	0.283	22.25
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.225	0.288	20.88
06-MC36-EF-1	fragment	SRI Lost Hat	2006	0.221	0.284	21.98
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.216	0.279	23.35
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.221	0.284	21.98
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.213	0.276	24.26
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.225	0.288	20.88
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.200	0.263	27.75
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.222	0.285	21.70
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.222	0.285	21.70
07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.204	0.267	26.65

## 2007 Channel Islands Peregrine Falcon Study Final Report

07-MC27a-EF-2	fragment	SRI Lobos Canyon	2007?	0.220	0.283	22.25
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## 2007 Channel Islands Peregrine Falcon Study Final Report

Appendix vi. Alpha Analytical Technical Standard Operating Procedures for Determination of PCB Homologs, Individual Congeners, and Pesticides by GC/MS – SIM.

## Determination of PCB Homologs, Individual Congeners, and Pesticides by GC/MS - SIM

References: Method 8082A Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Rev. 1, February 2007, Test Methods for Evaluating Solid Waste, SW-846

Method 8081B Organochlorine Pesticides by Gas Chromatography, Rev. 2, Update IV, Feb 2007, Test Methods for Evaluating Solid Waste, SW-846

Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007, Test Methods for Evaluating Solid Waste, SW-846.

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-10A

Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD), Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, January 1999, EPA/625/R-99/010b.

Method 680, "Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography / Mass Spectrometry", USEPA, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio; November 1985.

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### Uncontrolled Document

Prepared By:

Name: Elizabeth Porta

Position: Sediment/Tissue Product Line Manager

Signature: Elizabeth Porta

Date: 3/21/11

Authorized By:

Name: Joseph Watkins

Position: Laboratory/Technical Director

Signature: Joseph Watkins

Date: 3/21/11

### ISSUE AMENDMENTS

Changes since last issue:

References: Changed Method 8270C to 8270D

Section 1: Clarified extraction/cleanup methods.  
Section 2.1: Added method modifications  
Section 3: Edited concentration range for soil/sediment and tissue samples.  
Section 7.3: Clarified column type  
Section 7.6: Updated computer software version  
Section 8: Added criteria for spike solution assay  
Section 8.5: Added working solution dilution information.  
Section 8.8, 8.12.2 and 8.16: Concentrations adjusted  
Section: 9.8: Clarified method sequence  
Section 10.1.2: Removed tuning following 8270D criteria  
Section 10.1.4: GC Conditions clarified  
Section 10.1.6: LVI parameters clarified  
Section 10.2.3: Clarified sequence filename nomenclature.  
Section 10.2.4: Edited time window for calibration standards analysis.  
Section 10.2.9: ICV criteria updated to 8270D  
Section 10.3.3: Clarified generalized autosampler sequence information.  
Section 10.4.3 and 10.4.4: CCV criteria updated to 8270D  
Section 11.2 and 11.3: clarified Aroclor quantification  
Section 11.6: Removed references to data corrections for M+35 and M+70 ion interferences  
Section 11.11: Removed surrogate correction calculation  
Section 12: Table updated for Method change from 8270C to 8270D  
Section 16: Removed Tables III and IV  
Table 1: Edited Surrogate and IS References for 209 Congeners.  
Table 2: Removed Interference Check M+35 and M+70 information

## Determination of PCB Homologs, Individual Congeners, and Pesticides by GC/MS - SIM

- References: **Method 8082A** Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Rev. 1, February 2007, Test Methods for Evaluating Solid Waste, SW-846
- Method 8081B** Organochlorine Pesticides by Gas Chromatography, Rev. 2, Update IV, February 2007, Test Methods for Evaluating Solid Waste, SW-846
- Method 8270D**, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007, Test Methods for Evaluating Solid Waste, SW-846,
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-10A
- Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD), Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, January 1999. EPA/625/R-96/010b.
- Method 680**, "Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography / Mass Spectrometry", USEPA, Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio; November 1985

### 1. Scope and Application

**Matrices:** This method is applicable to the quantification of Polychlorinated Biphenyls (PCBs) as Homologs, Aroclors and/or individual Congeners as well as Pesticides in water, soil, sediment, tissue (either animal or vegetable) and in ambient air using PUF sampling followed by Gas Chromatography/Mass Spectrometry with Selected Ion Monitoring (GC/MS-SIM). This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are also identified and measured as isomer groups, homologs (*i.e.*, by level of chlorination)

**Definitions:** Refer to Alpha Analytical Quality Manual.

This method is applicable to the analysis and quantification of sample extracts for PCBs as single Congeners, Homologs and/or commercial Aroclors as well as Pesticides by Gas Chromatography/Mass Spectrometry with Selected Ion Monitoring (GC/MS-SIM). Target analytes include selected PCB congeners from BZ1 to BZ209, the Homolog groups, PCB Aroclors and Pesticides listed below. Analytes are determined and measured in the concentration range of 0.5 to 500 parts per trillion (ng/L) for water samples, 0.333 to 400 parts per billion (ug/Kg) for soil/sediment and tissue samples, and 5-500 ng/puf for PUF cartridges. Detection limits for Homolog groups are equal to the lowest detection limit of the individual congeners detected within that group. Detection limits will vary with the individual sample matrix, sample preparation procedures, instrument calibration range, and volume of sample analyzed. In general, analytes detected over these concentration ranges will be diluted and re-analyzed for accurate quantitation. Additionally, this method can provide a "total" PCB result for a given sample extract.

The following extraction and cleanup methods may apply, prior to sample analysis:

- *Extraction of Water Samples by Separatory Funnel-Method 3510C* (OP-001),
- *Tissue Preparation and Homogenization* (OP-003),
- *Shaker Table Extraction* (OP-013),
- *Sulfur Cleanup with Copper-Method 3660B* (OP-007),
- *Gel Permeation Chromatography-GPC* (OP-006)



- *Sulfuric Acid Cleanup-Method 3665A (OP-010),*
- *Silica Gel Cleanup (OP-014),*
- *Microscale Solvent Extraction – Method 3570 (OP-016)*
- *Soxhlet Extraction – Method 3540C (OP-019),*
- *Soxhlet Extraction of PUF Cartridges (OP-020)*

The existence of 209 possible PCB congeners makes it impractical to list each potential method analyte and Chemical Abstract Service (CAS) number. Because in some cases, depending upon client request, PCBs are identified and measured as isomer groups, the non-specific CAS number for each level of chlorination is used to describe the method analytes. See below for this listing.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the GC/MS and in the interpretation of GC/MS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

PCB Homolog Group	Formula	CAS #
Monochlorobiphenyl	C <sub>12</sub> H <sub>9</sub> Cl	27323-18-8
Dichlorobiphenyl	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub>	25512-42-9
Trichlorobiphenyl	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub>	25323-68-6
Tetrachlorobiphenyl	C <sub>12</sub> H <sub>6</sub> Cl <sub>4</sub>	26914-33-0
Pentachlorobiphenyl	C <sub>12</sub> H <sub>5</sub> Cl <sub>5</sub>	25429-29-2
Hexachlorobiphenyl	C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub>	26601-64-9
Heptachlorobiphenyl	C <sub>12</sub> H <sub>3</sub> Cl <sub>7</sub>	28655-71-2
Octachlorobiphenyl	C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub>	31472-83-0
Nonachlorobiphenyl	C <sub>12</sub> H <sub>1</sub> Cl <sub>9</sub>	53742-07-7
Decachlorobiphenyl	C <sub>12</sub> Cl <sub>10</sub>	2051-24-3

Pesticides	Formula	CAS #
4,4'-DDD	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub>	72-54-8
4,4'-DDE	C <sub>14</sub> H <sub>8</sub> Cl <sub>4</sub>	72-55-9
4,4'-DDT	C <sub>14</sub> H <sub>9</sub> Cl <sub>5</sub>	50-29-3
Aldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	309-00-2
Alpha-BHC	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	319-84-6
Alpha-Chlordane	C <sub>10</sub> H <sub>6</sub> Cl <sub>8</sub>	5103-71-9
Beta-BHC	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	319-85-7
Delta-BHC	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	319-86-8
Dieldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	60-57-1
Endosulfan I	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	959-98-8

Endosulfan II	C <sub>8</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	33213-65-9
Endosulfan Sulfate	C <sub>9</sub> H <sub>4</sub> Cl <sub>6</sub> O <sub>4</sub> S	1031-07-8
Endrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	72-20-8
Endrin Aldehyde	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	7421-93-4
Endrin Ketone	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	53494-70-5
Gamma-BHC (Lindane)	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	58-89-9
Gamma Chlordane	C <sub>10</sub> H <sub>6</sub> Cl <sub>8</sub>	5103-74-2
Heptachlor	C <sub>10</sub> H <sub>5</sub> Cl <sub>7</sub>	76-44-8
Heptachlor Epoxide	C <sub>10</sub> H <sub>5</sub> Cl <sub>7</sub> O	1024-57-3
Methoxychlor	C <sub>16</sub> H <sub>15</sub> Cl <sub>3</sub> O <sub>2</sub>	72-43-5

## 2. Summary of Method

An aliquot of a well mixed, homogeneous aqueous, solid, or tissue sample is accurately measured or weighed for sample preparation. Generally, 1L of water sample, 1-10g of tissue sample, 5-10g of sediment/soil sample for *Microscale Solvent Extraction - 3570 (OP-016)* and 15-30g of sediment/soil sample for *Soxhlet Extraction (OP-019, OP-020)*. The PUF cartridge is extracted via Soxhlet, with the appropriate solvent. Water, soil/sediment, and tissue samples as well as PUF cartridges are spiked with surrogate compounds and extracted using methylene chloride or a methylene chloride/acetone mixture. The extract is dried and exchanged to hexane during sample concentration to a 1-10mL final volume. If necessary, the sample may be copper cleaned to remove sulfur, and/or GPC, silica or acid cleaned to lessen sample matrix interferences, prior to sample analysis.

After cleanup, the extracts are spiked with internal standards, and analyzed by GC/MS-SIM. Analytes are introduced into the GC/MS by injecting a known volume of the calibration standards, quality control samples, and sample extracts into the GC equipped with a narrow-bore capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer operating in the selective ion mode (SIM). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of the calibration standards. Concentrations are determined using mean relative response factors from a multi-level calibration curve. Response factors for target analytes and surrogate compounds are determined relative to the internal standards. Multi-component analytes (PCB Homologs) are assigned the response factor of a representative PCB congener from that chlorination group. For PCB Aroclors single point calibration factors are used.

### 2.1 Method Modifications from Reference

This method exhibits some modification from the reference methods.

SIM data acquisition parameters, GC separation/operating conditions and MS sensitivity/calibration ratios for ions, and column type differ from the one described in Method 680 due to changes in technology since 1985.

Different compounds are utilized as Internal Standards and Surrogates than those specified in Method 680.

Different Calibration Congeners are used for Homologs group than the ones specified in Method 680.

Corrections are not made to any data for Homolog groups Cl<sub>2</sub> – Cl<sub>8</sub> for interferences resulting from M+35 or M+70 ions.

Acceptance criteria for ICAL, ICV, CCV, Surrogates and Internal Standards have been adopted from the guidance in Method 8270D,



Different DFTPP criteria then specified in method 8270D. Maximum Sensitivity Criteria are used.

### 3. Reporting Limits

Analytes are determined and measured in the concentration range of 0.5 to 500 parts per trillion (ng/L) for water samples, 0.333 to 400 parts per billion (ug/Kg) for soil/sediment and tissue samples, and 5-500 ng/puf for PUF cartridges. The detection limit for Homolog groups is equal to the lowest detection limit of the individual congener detected within that group. Detection limits will vary with the individual sample matrix, sample preparation procedures, instrument calibration range, and volume of sample analyzed.

### 4. Interferences

- 4.1 Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause interferences that lead to discrete artifacts and/or elevated baselines in the ion current profiles. Demonstrate that all of these materials are free from interferences under the conditions of the preparation and analysis by extracting and analyzing a laboratory method blank with each batch of up to 20 samples.
- 4.2 Contaminants co-extracted from the sample may cause matrix interferences. The extent of matrix interferences will vary considerably from sample to sample, depending upon the nature of the environment being investigated. An interference, which is unique to SIM techniques, can arise from the presence of co-eluting compounds, which contain the same quantification mass ion, or the same number of chlorine atoms. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantification ion and the confirmation ion are not within the specified limits, then interferences may be present. Quantification and confirmation ion criteria can be found in Table II.
- 4.3 With the isomer, or Homolog group quantification approach, co-eluting PCBs that contain the same number of chlorines, are identified and measured together. Therefore, co-eluting PCBs are only a problem if they contain a *different* number of chlorine atoms.
- 4.4 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences or carryover. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed.

### 5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

## 6. Sample Collection, Preservation, Shipping and Handling

### 6.1 Sample Collection

**Aqueous samples:** Collect in 1L or 2L amber glass bottles. The minimum amount of sample needed to reach the reporting limits in Section 3.0 for this method for aqueous samples is 1L. Additional sample is needed (approximately 3X the minimum amount) if MS/MSD analyses are to be performed.

**Soil/sediment samples:** Collect in glass soil jars. The minimum amount of sample needed to reach the reporting limits in Section 3.0 for this method for solid and tissue matrices is 5g. Additional sample is needed (approximately 3X the minimum amount) if MS/MSD analyses are to be performed.

**Air Samples:** Collected with appropriate air sampling techniques described in the Reference Method for collecting PUF cartridge air samples.

### 6.2 Sample Preservation

**Aqueous samples:** Store without preservative at 4°C.

**Soil/sediment samples:** Stored at 4°C, or if desired, frozen.

**Air Samples:** Stored at 4°C without preservation.

### 6.3 Sample Shipping

No special shipping requirements.

### 6.4 Sample Handling

The hold time for this method is 7 days for the extraction of aqueous samples and 14 days for the extraction of solid and tissue samples. If sediment or tissue samples are frozen, this suspends the holding time until removal from the freezer. Air PUF cartridges must be extracted within 7 days of collection.

All extracts must be analyzed within 40 days of the extraction date.

## 7. Equipment and Supplies

**7.1 Gas Chromatograph:** The instrumentation includes a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for splitless injection onto a capillary column. The injection port includes a silanized glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination. The model is HP6890 or equivalent. The injection port will require maintenance on an as needed basis if degradation or contamination is apparent.

**7.2 Large volume injector, PTV - Gerstel, or equivalent:** Temperature and flow programmable and capable of injecting 1 to 50  $\mu$ L of standards and sample extracts onto the GC column in a split or splitless mode.



**7.3 Column:** For 209 Congener and Homolog Analysis - Restek 60-m x 0.18 mm ID, 0.18 um film thickness, fused-silica capillary column with Crossbond phase, or equivalent.

For 136 Congener, Homolog, Pesticide Analysis – Restek 60-m x 0.25 mm ID 0.25 um film thickness, fused-silica capillary column with Crossbond phase, or equivalent.

**7.4 Mass Spectrometer:** The mass spectrometer must operate at 70ev (nominal) electron energy in the electron impact ionization mode and be tuned to optimize the sensitivity of the instrument to the maximum in the mass range being monitored (45 - 525 amu). The GC capillary column is fed directly into the ion source of the mass spectrometer. The model is HP5973, or equivalent. The source will require cleaning and/or filament replacement on an as needed basis. Please refer to the instrument hardware manual, located in the laboratory, for detailed procedures.

**7.5 Auto sampler:** Adapted onto the Gas Chromatograph. The model is HP 6890 series autosampler with a GC autosampler controller, or equivalent.

**7.6 Computer:** With Windows XP operating software utilizing HP Enviroquant G1701DA Version D.01.02 software; Audit Trail: audit.txt function is used for audit trail purposes.

**7.7 Helium:** Ultra high purity grade (99.9999% pure) or hydrogen of equivalent purity.

## 8. Reagents and Standards

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. See SOP Reagent, Solvent, and Standard Control (G-008) for additional details regarding solvent purity. All solvent expirations determined as indicated by manufacturer guidelines

Analytical Standards are stored according to manufacturer's recommended procedure. Stock standards, and calibration curve standards are stored in either 10mL or 40mL glass vials and kept in a standards freezer at  $-10^{\circ}$  –  $-20^{\circ}\text{C}$  in the GC Instrumentation Lab. Primary standards are discarded as indicated by the vendor expiration. Stock standards are given one year expiration from the preparation date or the expiration of the primary vendor solution, whichever occurs first. Working standards are given six month expiration from the preparation date or the expiration of the primary solution which ever occurs first. If breakdown of a solution is observed the solution will be discarded. All analytical standards are prepared in Hexane. All extraction standards (surrogates, laboratory control spikes and matrix spikes) are prepared in Acetone or methylene chloride for Soxhlet extraction - *Method 3540C*. All spiking solutions must be assayed for use by analysis before release to the preparation lab. Recoveries of 90% of the analytes must be +/- 20% of the true values. The remaining 10% must be +/- 30%. If there is a significant amount of spiking solution remaining after the six-month period, the lab will re-QC the solution. If the QC of the solution still passes the lab will extend the expiration date by another month.

**8.1 Methylene Chloride:** ACS approved, Pesticide grade, see SOP *Reagent, Solvent, and Standard Control* (G-008) for additional details regarding solvent purity.

**8.2 Acetone:** ACS approved, Pesticide grade, see SOP *Reagent, Solvent, and Standard Control* (G-008) for additional details regarding solvent purity.

- 8.3 Hexane:** ACS approved, Pesticide grade, see SOP *Reagent, Solvent, and Standard Control* (G-008) for additional details regarding solvent purity.
- 8.4 Methanol:** Purge and Trap grade, see SOP *Reagent, Solvent, and Standard Control* (G-008) for additional details regarding solvent purity.
- 8.5 DFTPP (decafluorotriphenylphosphene) tuning solution:** Prepare by diluting 0.025mLs of a 2000 ug/mL standard into 10mL of Methylene Chloride for a 5 ug/mL tuning standard. Working solution is further diluted 1:10 prior to analysis.
- 8.6 Individual Analytes (BZ-1 to BZ-209) and pesticides:** Obtained from AccuStandard or equivalent at a concentration of 100 ug/mL.
- 8.7 209 Congeners Custom Calibration Set:** Obtained from Accustandard as 9 separate mixes at the concentration of 10 ug/mL each. The solution consists of 209 Congeners. Prepare the Stock Solution by diluting the calibration mixes to a stock concentration of 1000 ng/mL. See Section 8.16 for calibration preparation information.
- 8.8 Custom 136 PCB Congeners Set/ Homolog Custom Mix, Retention Time Window / Calibration Standard:** Obtained from Accustandard as 7 separate mixes at the concentration of 4 ug/mL each. The solution consists of at least one representative PCB congener used for quantitation from each Homolog group and the first and last eluting congener of each Homolog group used to identify the start and stop time of each SIM window. Prepare the Stock Solution by diluting the calibration mixes and the Carbon-labeled Surrogate Stock solution to a 136 Cong/Surr Stock concentration of 400 ng/mL. See Section 8.16 for calibration preparation information.
- 8.9 Surrogates:** 4,4'-Dibromooctafluorobiphenyl (DBOB) and BZ 198, obtained from Ultra Scientific or equivalent.
- 8.9.1 DBOB/BZ198 stock solution:** Add 25 uL of the 5000 ug/mL DBOB primary solution and 1250 uL of the 100 ug/mL BZ 198 primary solution to 25 mL volumetric flask and dilute with hexane for 5000 ug/L stock solution. All compounds must be within 20% of their true value. 1mL is spiked into each QC and field sample. The concentrations may be adjusted to meet project specific needs.
- 8.9.2 Pest/Cong Surrogate spiking solution:** add 4 mL of DBOB/BZ198 stock solution to 200 mL volumetric flask and dilute with acetone, for a 100 ug/L final concentration. The solution must be assayed for use by analysis before release to the preparation lab. All compounds must be within 20% of their true value. 1mL is spiked into each QC and field sample. The concentrations may be adjusted to meet project specific needs.
- 8.10 Carbon-labeled Surrogates:** BZ 19 and BZ 202, obtained from Cambridge Isotope or equivalent, at a concentration of 40 ug/mL.
- 8.10.1 Carbon-labeled Surrogates Stock Solution:** Prepare a separate solution by taking 1.25mL of each of the 40 ug/mL surrogate solutions, and add to 10mL of hexane for a stock concentration of 5 ug/mL or 5000 ng/mL.
- 8.10.2 Homolog Surrogate spiking solution:** Add 250 uL of each surrogate to 250 mL volumetric flask and dilute with acetone, for a 40 ug/L final concentration. All

compounds must be within 20% of their true value. 1mL is spiked into each QC and field sample. The concentrations and the spiking amount may be adjusted to meet project specific needs.

NOTE: PCB Homolog Surrogate spiking solution for Soxhlet extraction should be prepared in methylene chloride.

- 8.10.3 High Homolog Surrogate spiking solution:** Add 1.25 mL of each surrogate to 50 mL volumetric flask and dilute with methylene chloride, for a 1000 ug/L final concentration. The solution must be assayed for use by analysis before release to the preparation lab. All compounds must be within 20% of their true value. 1mL is spiked into each QC and field sample. The concentrations and the spiking amount may be adjusted to meet project specific needs.

NOTE: PCB High Homolog Surrogate spiking solution is prepared in methylene chloride and used for Soxhlet extraction only.

- 8.11 Carbon-labeled Internal Standards (IS):** BZ 15 and BZ 180, obtained from Cambridge Isotope or equivalent, at a concentration of 40 ug/mL. Add 2.5mL of each internal standard to 10mL volumetric flask and dilute with hexane, for a final concentration of 10 ug/mL. 20uL is spiked into each standard, QC sample, and field sample. The resulting on-column concentration is 200 ug/L in a 1mL sample aliquot. The concentrations may be adjusted to meet project specific needs.

- 8.12 PCB and Pesticide Laboratory Control Sample, Matrix Spike, and Matrix Spike Duplicate (LCS/MS/MSD):** A solution of at least 10 PCB congeners, one from each Homolog group, from a source other than that of the calibration standards (Ultra Scientific or equivalent, 4 mixes at 4 ug/mL each.

- 8.12.1 Homolog LCS spiking solution:** Add 1 mL of each mix to 100mL volumetric flask and dilute with *Acetone*, for a 40 ug/L final concentration. The solution must be assayed for use by analysis before release to the preparation lab. Recoveries of 90% of the analytes must be +/- 20% of the true values. The remaining 10% must be +/- 30%. 1mL is spiked into the LCS and each designated MS/MSD field sample. The specific PCB congeners or Pesticides as well as concentration and spiking amount may be adjusted to meet project specific needs.

NOTE: PCB Homolog LCS/MS/MSD spiking solution for Soxhlet extraction should be prepared in methylene chloride.

- 8.12.2 High Homolog LCS spiking solution:** Add 2.5 mL of each mix to 25 mL volumetric flask and dilute with acetone or methylene chloride, for a 400 ug/L final concentration. The solution must be assayed for use by analysis before release to the preparation lab. Recoveries of 90% of the analytes must be +/- 20% of the true values. The remaining 10% must be +/- 30%. 1mL is spiked into the LCS and each designated MS/MSD field sample. The specific PCB congeners or Pesticides as well as concentration and spiking amount may be adjusted to meet project specific needs.

NOTE: HIGH Homolog LCS/MS/MSD spiking solution is prepared in methylene chloride and used for Soxhlet extraction only.

- 8.13 Independent Calibration Verification (ICV) standard:** This is a source separate from the calibration curve containing at least 50% of all targeted calibration, individual, and



retention time window congeners of interest. (Ultra Scientific or equivalent) Prepare a standard level at or near the mid calibration point. Spike 1 mL with 20uL of the internal standard in 8.11, above, prior to analysis.

**8.14 SRM 1944/1941b – New York/New Jersey Waterway Sediment, and SRM 1974b – Organics in Mussel Tissue:** From National Institute of Standards & Technology (NIST). Please refer to the individual certifications for the assigned true values. These SRMs may be extracted and analyzed with sample batches as part of the overall QC evaluation, if requested by the client. Other certified SRMs may be used on a project specific basis.

**8.15 Aroclors Solution:** Obtained from Ultra at a concentration of 100 ug/mL for one-point calibration.

### 8.16 Calibration Preparation Information

<u>Homolog Calibration Congener</u>	<u>Isomer Group</u>	<u>Stock Conc. ng/mL</u>
BZ 1 (1 <sup>st</sup> Mono)	CI1	400 ng/mL
BZ 8, BZ 5/8	CI2	400 ng/mL
BZ 29	CI3	400 ng/mL
BZ 50	CI4	400 ng/mL
BZ 87, BZ 87/111	CI5	400 ng/mL
BZ 154	CI6	400 ng/mL
BZ 188 (1 <sup>st</sup> Hepta)	CI7	400 ng/mL
BZ 200, BZ 200/204	CI8	400 ng/mL
BZ 206 (last Nona)	CI9	400 ng/mL
BZ 209 (Deca)	CI10	400 ng/mL
<u>Add'l Ret. Window PCB Isomer Group</u>	<u>Stock Conc. ng/mL</u>	
<b><u>Congeners</u></b>		
BZ 3 (last Mono)	CI1	400 ng/mL
BZ 10 (1 <sup>st</sup> Di)	CI2	400 ng/mL
BZ 15 (last Di)	CI2	400 ng/mL
BZ 19 (1 <sup>st</sup> Tri)	CI3	400 ng/mL
BZ 37 (last Tri)	CI3	400 ng/mL
BZ 54 (1 <sup>st</sup> Tetra)	CI4	400 ng/mL
BZ 77 (last Tetra)	CI4	400 ng/mL
BZ 104 (1 <sup>st</sup> Penta)	CI5	400 ng/mL
BZ 126 (last Penta)	CI5	400 ng/mL
BZ 155 (1 <sup>st</sup> Hexa)	CI6	400 ng/mL
BZ 169 (last Hexa)	CI6	400 ng/mL
BZ 189 (last Hepta)	CI7	400 ng/mL
BZ 202 (1 <sup>st</sup> Octa)	CI8	400 ng/mL
BZ 205 (last Octa)	CI8	400 ng/mL
BZ 208 (1 <sup>st</sup> Nona)	CI9	400 ng/mL
<b><u>Surrogates</u></b>		
DBOB	N/A	5000 ng/mL
BZ 198	CI8	5000 ng/mL
<b><u>Carbon-labeled Surrogates</u></b>		
BZ 19	CI3	5000 ng/mL
BZ 202	CI8	5000 ng/mL

**Note:** Any of the above congeners may be reported as individual congeners, as well as within a Homolog group, as this method is not limited to this congener list. Additional congeners may be

analyzed via this method by utilizing the MDL and PQL from a congener of the same Homolog class that has been previously established. Parentheses indicate the first and last eluting PCB congener in each chlorination level, used to establish the selective ion monitoring (SIM) retention time windows.

<b>Pesticide</b>	<b>Stock Conc. ng/mL</b>
Methoxychlor	2000 ng/mL
4,4'-DDD	2000 ng/mL
4,4'-DDE	2000 ng/mL
4,4'-DDT	2000 ng/mL
Aldrin	2000 ng/mL
Alpha-BHC	2000 ng/mL
Alpha-Chlordane	2000 ng/mL
Beta-BHC	2000 ng/mL
Delta-BHC	2000 ng/mL
Dieldrin	2000 ng/mL
Endosulfan I	2000 ng/mL
Endosulfan II	2000 ng/mL
Endosulfan Sulfate	2000 ng/mL
Endrin	2000 ng/mL
Endrin Aldehyde	2000 ng/mL
Endrin Ketone	2000 ng/mL
Gamma-BHC (Lindane)	2000 ng/mL
Gamma Chlordane	2000 ng/mL
Heptachlor	2000 ng/mL
Heptachlor Epoxide	2000 ng/mL

#### **Suggested Curve Preparation for Individual Components (Minimum 5 Levels)**

<b>Calibration Level</b>	<b>Surr. Stock 5000ng/mL</b>	<b>209 Cong. Stock 1000ng/mL</b>	<b>136 Cong. /Surr Stock 400ng/mL</b>	<b>Calibration L6 (200ug/L)</b>	<b>Final Volume</b>
L1 – 0.5 ug/L	-	-	-	0.025mL	10 mL
L2 – 1.0 ug/L	-	-	-	0.05mL	10 mL
L3 – 10 ug/L	-	-	-	0.5mL	10 mL
L4 – 20 ug/L	-	-	-	1mL	10 mL
L5 – 50 ug/L	0.1mL	0.5mL	1.25mL	-	10 mL
L6 – 200ug/L	0.4mL	2mL	5mL	-	10 mL
L7 – 400 ug/L	-	-	-	-	10 mL
L7 – 500 ug/L	1mL	5mL	-	-	10 mL

**Note:** 20 uL of the 10 ug/mL chosen Internal Standard mix is added to each calibration level for a concentration of 200 ng/mL. A minimum of a 5-level curve must be analyzed, but 6-levels, or more, may be analyzed and evaluated depending upon client specific project detection limits.

## **9. Quality Control**

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

Quality Control (QC) samples are necessary to monitor both the sample extraction and instrument analysis procedures. The Quality Control samples described below are considered the method



defaults, and are the minimum requirements, except where noted. Client and Project specific Data Quality Objectives (DQOs) supersede the requirements in this section where applicable. Client or Project specified DQOs shall be included, or referenced, in the final report to the client.

### 9.1 Blank(s)

A method blank must be extracted (spiked with surrogates and internal standards) and analyzed once per every 20 samples or per extraction batch, whichever is more frequent.

An *acceptable* method blank should not contain any individual compound at the concentration of reporting limit, or above. All efforts must be made to identify and eliminate the source of contamination. The presence of analytes at concentrations at or above the reporting limit will warrant application of a "B" qualifier to that target compound(s) on all associated report forms, and perhaps re-extraction of all associated samples. The results are qualified with a "B" for any associated sample concentrations that are less than 5x the blank concentration for the analyte. Surrogate and internal standard recoveries must meet the QC limits for the method blank, see Sections 9.7.1 and 9.7.2. Re-extraction *corrective action* that would exceed the sample holding time criteria should be discussed with the client, Laboratory Director, QA Manager, and/or Section Supervisor prior to implementation. Exceptions may be made with approval of the Section Supervisor if the samples associated with an out of control method blank are non-detect for the affected compound(s) or if the concentrations of the affected compound(s) are greater than 5x the blank level in the samples. In such cases, the sample results are accepted without corrective action for the high method blank result. The client must be notified, via the project narrative, of any method blank non-compliance associated with the sample results.

### 9.2 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

The laboratory control sample/laboratory control sample duplicate (LCS/LCSD) contains at least 10 PCB congeners that represent each Homolog group. If only PCB Congeners are being evaluated, and if the list includes more than 20 congeners, at least 16 individual congeners will be spiked. If pesticides are being analyzed, the analyte list targeted in most cases will be spiked into the LCS/LCSD. The LCS/LCSD is extracted along with the samples. An LCS/LCSD pair must be extracted and analyzed once per every 20 samples or per extraction batch, whichever is more frequent. The number of PCB congeners in this sample may vary with client specific requests.

The acceptable recovery QC limits are found in Section 12 for an aqueous, solid, tissue and PUF LCS/LCSD.

Corrective Action: Repeat analysis or check to see if an analytical error has occurred. If the LCS recovery is still out of control, re-extract and re-analyze the LCS/LCSD and all associated samples. Samples cannot be analyzed until an acceptable LCS/LCSD is obtained. Exceptions may be made with approval of the Section Supervisor if the samples associated with the out of control LCS/LCSD are also associated with a matrix spike and matrix spike duplicate that is in control which demonstrates an isolated problem pertaining to the LCS and/or LCSD only. An explanation of this out of control LCS and/or LCSD recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS/MSD results as batch QC.

### 9.3 Initial Calibration Verification (ICV)

Refer to section 10.2.4

## 9.4 Continuing Calibration Verification (CCV)

Refer to section 10.4

## 9.5 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

Matrix spike and matrix spike duplicate analyses are performed at the client's request.

The acceptable recovery and RPD QC limits are found in Section 12 for an aqueous, solid, tissue, and PUF MS/MSDs.

Corrective Action: Repeat analysis or check to see if an analytical error has occurred. If the % recovery or %RPD still exceeds the control limits and the associated LCS/LCSD is within control, include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy or precision of the affected results as evidenced by the matrix spike and matrix spike duplicate exceedance.

## 9.6 Laboratory Duplicate

Laboratory matrix or sample duplicates are analyzed if requested by the client. The QC limit is 30% RPD for target compounds found above 5 times the reporting limit.

Corrective Action: If the %RPD exceeds the 30% control limit and the associated MS/MSD %RPD is within 30%, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results isolated to this sample, as evidenced by the matrix duplicate exceedance and the MS/MSD acceptance. If both the sample/duplicate and the MS/MSD exceed the control limits, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results as evidenced by the sample/duplicate and the MS/MSD exceedences.

## 9.7 Method-specific Quality Control Samples

### 9.7.1 Surrogates

Surrogates are monitored for recovery for all matrices. The recovery limits are found in Section 12.

Corrective Action: Check to see if an analytical or dilution error occurred and re-calculate. If only one surrogate falls below the recovery limit, but is above 10% recovery, the exceedance is noted, with approval of the Section Supervisor, and the results are reported to the client with a notation in the case narrative. If all surrogates are recovered below the limit, re-extract the sample and report the re-extract results along with the original results, if re-extraction occurred beyond the holding time, and the re-extract surrogates are within the QC limits. If the surrogates are recovered below the limit in the re-extract, this confirms a suspected matrix interference on the surrogates, and only the original analysis needs to be reported. If the chromatogram shows obvious matrix interference, no re-analysis or re-extraction is necessary. This decision must be made with approval of the Section Supervisor. Surrogate outliers and sample re-extracts must be noted in the case narrative to the client.

### 9.7.2 Internal Standards

Internal standards are added to every field sample, QC sample, standard, and method blank. The acceptance limits are -50% to +100% of the internal standard response (or area) of the daily continuing calibration verification standard.

Corrective Action: Check to see if an analytical, dilution, or spiking error occurred. If the chromatogram shows obvious matrix interference, no re-analysis is necessary. *This decision must be made with approval of the Department Manager.* Note the exceedance in the case narrative to the client. If no obvious interference is present, re-analyze the extract. If internal standards are now within the acceptance limits, report only the re-analysis, as long as the re-analysis occurred within the 40-day analytical hold time. If the re-analysis occurred outside of the 40-day analytical hold time, both the original and re-analysis must be reported. If the internal standards again are outside the acceptance limits, after re-analysis, either within or outside of the 40-day hold time, report only the original analysis, and include a narrative to the client that the suspected matrix interference on the internal standards was confirmed by sample re-analysis.

#### 9.7.3 Standard Reference Materials

Standard reference materials (SRMs) are available from the National Institute of Standards and Technology (NIST) and are extracted and analyzed with samples on a project specific basis. These are not used as controls, but to evaluate potential matrix effects in associated samples for the target compounds being evaluated.

Acceptance criteria for SRM analysis will vary from project to project depending upon client data quality objectives (DQOs). Generally, 40% - 140% recovery of the true certified values of the target compounds of interest, serves as advisory acceptance criteria.

Corrective Action: Repeat analysis and/or check to see if an analytical error has occurred. If the % recovery or %D still exceeds the control limits and the associated LCS/LCSD and/or MS/MSD are within control, include a project narrative with the results to the client noting that the observed recovery exceedances of the SRM are isolated to this sample as evidenced by the LCS/LCSD and/or MS/MSD acceptance.

- 9.7.4 **PEM Evaluation for Pesticide analysis only:** Evaluate the percent degradation of 4,4'-DDT (to 4,4'-DDE and 4,4'-DDD) and Endrin (to Endrin Aldehyde and Endrin Ketone) to monitor the integrity of the injection system (see Section 11.21 for calculation). Degradation is not considered to be a problem if the percent degradation of 4,4'-DDT and Endrin are less than 20%. If either compound does exceed 20% breakdown, the analysis must be stopped, the injection port serviced and other maintenance may need to be performed.

## 9.8 Method Sequence

Tune	– (0.5 ug/mL) full scan using DFTPPBNA.m
CCV	– (50 ng/mL) using 136BNA5.m or PCB209BNA2
Method Blank	– (ID from sample preparation batch)
LCS	– (ID from sample preparation batch)
LCSD	– (ID from sample preparation batch)
Samples (up to 12-18 hours of analytical time)	
Tune	– 0.5 ug/mL) full scan using DFTPPBNA.m
CCV	–(50 ng/mL) using 136BNA5.m or PCB209BNA2
Samples (up to 12-18 hours of analytical time)	



CCV – (50 ng/mL) 136BNA5.m or PCB209BNA2

## 10. Procedure

### 10.1 Equipment Set-up

Prior to the analysis of any standards or samples, the instrument acquisition and processing methods must be set up. This includes the GC run parameters and the SIM mode acquisition ion entries into the different SIM acquisition retention time windows. An initial calibration must be analyzed to establish linearity of the instrument. First, the mass spectrometer must be tuned to the meet the abundance criteria for PFTBA when using maximum sensitivity tuning.

#### 10.1.1 PFTBA Manual Tuning

**10.1.1.1** Prior to initial calibration tune the mass spectrometer using PFTBA (Perfluorotributylamine - calibration gas) to maximize the sensitivity of the instrument in the mass range of interest, 45-525 amu. The use of PFTBA for MS tuning maximizes the sensitivity of the analysis within the mass/charge (m/e) range being monitored. *If only the PTFBA tune is required, per client request or project specific DQOs, the DFTPP tune in Section 10.1.2 does not need to be evaluated.*

**10.1.1.2** To acquire the PFTBA Tune:

- Click on the "Instrument" icon to open the ChemStation.
- Go into "Instrument Control" in the "GC/MS Top Environmental" screen.
- Go to "View" and select "Manual Tune".
- Go to "File" and select "Load Tune Values". Select the ATUNE.U file.
- Go back into "File" and select "Generate Report". The calibration gas will automatically turn ON, equilibrate for approximately 20 seconds, and generate a report. Evaluate the PFTBA tune against the parameters below.

PFTBA Ion	Relative Abundance
m/e 69	Base Peak with > 150,000 counts
m/e 219	40% to 90% of Base Peak
m/e 502	4% to 10% of Base Peak

If the PFTBA tune meets the criteria, "Save" the tune values, and exit the program.

**10.1.1.3** If the PFTBA does not meet the criteria above, an experienced mass spectrometrist may attempt the following corrective actions:

- Adjust the ion focus value up or down while the calibration gas valve is open and continue to scan until the desired abundances are achieved.
- Adjust the entrance lens value up or down while the calibration gas valve is open and continue to scan until the desired abundances are achieved.
- Save the tune parameters under PFTBA.U.

**10.1.2 DFTPP Tuning:** If only DFTPP is required, per client request or project DQOs, PFTBA does not need to be evaluated.

**10.1.2.1** Before the analytical standards are analyzed, the mass spectrometer must be evaluated for the proper ion criteria for DFTPP (decafluorotriphenylphosphene), if specifically requested by the client or included in a project specific QAPP. Generally, 1uL of a 500 ng/mL solution is evaluated. A larger volume or lesser concentration may be evaluated if using large volume injections. . If the instrument has been adjusted for the maximum sensitivity PFTBA, then the criteria in Section 10.1.2.6 applies. *DFTPP must be injected under full scan mode.*

**10.1.2.2** To acquire the DFTPP tune:

- Click on the "Instrument" icon to open the Chem Station, if not already open.
- Go into the "GC/MS Top Environmental" screen.
- Go into "Sequence."
- Edit the "Sample Table Log" by entering the "Vial" number starting at position 1, the "Data File ID" the acquisition method, DFTPPBNA.m, and finally the "Sample Name" (i.e., "DFTPP 0.5 ug/mL") When complete, click "OK".
- Go back into "Sequence" and "Save" the sequence as the date, such as, S2060501.s. The ending "01" indicates the first sequence created on 06/05. The first number comes from instrument ID, i.e. BNA2.
- Go back into "Sequence" and "Load and Run" the sequence that was just saved.

**10.1.2.3** After the analysis of the DFTPP, evaluate the tune as follows:

- Enter into the "Environmental Data Analysis" (off-line) screen.
- Go to "File" and select the tune data file.
- Go into "Tuner" and select "Eval DFTPP", then select "AutoFind DFTPP to Screen," to evaluate the tune file, based on the pre-set SW-846 criteria. The software will evaluate the tune by selecting three scans of the DFTPP peak and will display the ion intensities on the screen. That is, one scan at the apex, one scan directly preceding the apex and one scan following the apex and averages them, then takes one background subtracted scan, 20 seconds before the beginning of the DFTPP peak. If the criteria below are met, repeat, but select "AutoFind to Printer", for a hardcopy of the tune evaluation for the record.

**Note:** the Maximum Sensitivity tune must be evaluated using the correct method to ensure the criteria in Section 10.1.2.6 are met.

**10.1.2.4** If the "AutoFind" tune evaluation does not meet the criteria below, manual evaluation of the tune can be performed by attempting either of the options below:

- Blow up the DFTPP peak on the screen and select either one single scan at the apex of the peak, or a scan immediately preceding or following the apex. Go into "Tuner" and select "Evaluate DFTPP to Screen," or "Evaluate DFTPP to Printer," as described above, OR,
- Take the average of the scans across the entire peak. Go into "Tuner" and select "Evaluate DFTPP to Screen," or "Evaluate DFTPP to Printer," as described above.

- 10.1.2.5** "Maximum Sensitivity" DFTPP is used for the analysis of PCB Congeners by GC/MS. It shows high-end sensitivity for the higher molecular weight ions that are present in, and evaluated for, PCBs.

**DFTPP KEY MASSES AND ABUNDANCE CRITERIA**  
**(Maximum Sensitivity)**

Mass      m/e Abundance criteria

51	N/A
68	N/A
70	N/A
127	30-80 percent of mass 198.
197	Less than 3 percent of mass 198.
198	Greater than 40 percent of mass 442.
199	5-15 percent of mass 198.
275	15-50 percent of mass 198.
365	Greater than 3 percent of mass 198.
441	Present but less than mass 443.
442	Base peak, 100 percent relative abundance.
443	18-30 percent of mass 442.

- 10.1.2.6** Tune acceptance must be verified at the beginning of every analytical shift, and prior to the analysis of any standards, and again at the beginning of each 12-18 hour tune clock as defined by the injection time of each DFTPP analysis. If the DFTPP tune does not meet the criteria above, the PFTBA must be re-evaluated, and adjustments made by an experienced mass spectrometrists, to obtain an acceptable DFTPP tune, before continuing with any analysis.

**10.1.3 PEM Evaluation – only if Pesticides are targets of interest**

- 10.1.3.1** Prior to initial calibration and at the start of each run a PEM must be analyzed and evaluated as mentioned above in the quality control section 9.7.4.

**10.1.4 GC Instrumental Conditions**

- 10.1.4.1** For 136 Congener, Homologs, Pesticide Analysis Inject an aliquot of 1uL to 5uL into the capillary column of the gas chromatograph at the following conditions. Injection volume (using the Large Volume Injector, LVI) amount will be dictated by project specific DQOs.

<b>GC Parameter</b>	<b>Setting</b>
Injector Temp:	70 - 300 °C
Transfer Line Temp:	280 °C
Initial Oven Temp:	50°C
Initial Hold Time:	2.5 minutes
Ramp Rate 1:	25 °C / minute



<i>Final Temperature 1:</i>	180 °C
<i>Final Hold Time 1:</i>	0 minute
<i>Ramp Rate 2:</i>	3 °C / minute
<i>Final Temperature 2:</i>	250 °C
<i>Final Hold Time 2:</i>	0 minute
<i>Ramp Rate 3</i>	15 °C / minute
<i>Final Temperature 3:</i>	300 °C
<i>Final Hold Time 3:</i>	11 minutes
<i>Total runtime:</i>	45.37 minutes
<i>Mode:</i>	Splitless / Constant Flow
<i>Purge:</i>	25 mL / minute – on at 2.5 minutes
<i>MS Temperature:</i>	250 °C, MS Source, 170 °C, MS Quad

- 10.1.4.2** For 209 Congener and Homolog Analysis inject an aliquot of 1uL to 5uL into the capillary column of the gas chromatograph at the following conditions. Injection volume (using the Large Volume Injector, LVI) amount will be dictated by project specific DQOs.

<b>GC Parameter</b>	<b>Setting</b>
<i>Injector Temp:</i>	70 - 300 °C
<i>Transfer Line Temp:</i>	300 °C
<i>Initial Oven Temp:</i>	65°C
<i>Initial Hold Time:</i>	2.1 minutes
<i>Ramp Rate 1:</i>	25 °C / minute
<i>Final Temperature 1:</i>	170 °C
<i>Final Hold Time 1:</i>	0 minute
<i>Ramp Rate 2:</i>	3 °C / minute
<i>Final Temperature 2:</i>	290 °C
<i>Final Hold Time 2:</i>	15 minutes
<i>Total runtime:</i>	61.3 minutes
<i>Mode:</i>	Splitless / Constant Pressure
<i>Purge:</i>	25 mL / minute – on at 2.00 minutes
<i>MS Temperature:</i>	250 °C, MS Source, 170 °C, MS Quad

### 10.1.5 Mass Spectrometer Conditions

The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the SIM mode using appropriate retention time windows to include the quantification and confirmation ions for each congener and the interference ions as shown in Table II.

### 10.1.6 Large Volume Injection (LVI) Parameters

<b>Gerstel *</b>	<b>Settings*</b>
Injector Temp:	70 - 300 °C
Initial Hold Time:	30 sec. - 3 minutes
Flow Rate:	0.5 - 5.0 mL / minute
Purge:	25 mL / minute – on at 2.00 minutes
Injection Volume:	1uL - 5uL

\* = The settings listed may vary from project to project, based on client specific DQOs. *Injection temperature, hold time, flow rate, purge time, and injection volume can affect chromatographic resolution and detection limits.* All parameters listed above can be set within the above setting ranges. Only a trained and experienced mass spectrometrists has the authority to change any setting. All standards and samples must be acquired using the same set of parameters. If any parameters are changed, a new initial calibration must be analyzed and accepted before any samples can be analyzed.

### 10.1.7 Data Acquisition Parameters

**10.1.7.1** SIM Windows must be set up that bracket the expected retention times for each target analyte. These windows include the quantitation (primary) and confirmation ions for each congener Homolog group. To establish the expected retention time window ranges, the mid-level retention time window standard containing the first and last eluting congener in each Homolog group, must be analyzed in full scan mode. The resulting full scan analysis will dictate the windows in which the selected ions will be monitored. Depending upon the length of the analytical GC column, the time each window is selectively monitored may vary. The retention time windows must be shifted accordingly, when instrument maintenance is performed, (*i.e.*, the column is clipped).

**10.1.7.2** The "dwell" time for each window should be set to 20 and the resolution should be set to "high." For pesticides it is set to "low".

## 10.2 Initial Calibration

**10.2.1** Before analysis of sample extracts, establish a multi-point response factor calibration curve showing the linear range of the analysis for all target analytes in Table II. Use at least 5 levels of standard concentrations at 0.5, 1.0, 10, 20, 50, 200, and 500 or 400 ng/mL to construct the curve. See Section 8.16 for the preparation of the standard solutions for the initial calibration curve.

**10.2.2** For PCB Aroclors single point calibration factors are used. The response of each individual peak in the sample is compared to a calibration standard to determine the analyte concentration in the sample. Using the GC system software, the analyst must choose 3-5 peaks from the pattern which are characteristic for the Aroclor to obtain the response for the component of interest. The peak area is calculated against the mass injected to

obtain a Calibration Factor. Calibration Factors are determined for individual peaks. The calibration factors are then used to calculate the concentration of each corresponding peak in the sample. The 3 to 5 resulting concentrations are averaged to provide the final result for the aroclor for the sample.

**10.2.3** Construct an analytical sequence using the HP Enviroquant software:

- Click on the "Instrument" icon to open the ChemStation
- Go into the "GC/MS Top Environmental" screen
- Go into "Sequence"
- Edit the "Sample Table Log" by entering the "Vial" number starting at position 1, the "Data File ID", the acquisition method (such as, 136CONGBNA5.m, which indicates the type of method and the instrument ID), and finally the "Sample Name" (such as, "I206051001STD0.5", for the first standard concentration level, etc.). When complete, click "OK".
- Go back into "Sequence" and "Save" the sequence as the date, such as, S2060501.s. The ending "01" indicates the first sequence created on 06/05. The first number comes from instrument ID, i.e. BNA2.
- Go back in to "Sequence" and "Print" the sequence that was just saved. This will become part of the instrument run log. See Section 11.0 for additional instrument run log details.
- Go back into "Sequence" and "Load and Run" the sequence that was just saved.

**10.2.4** When the sequence has finished running, the Enviroquant software will generate "Not Reviewed" quantitation reports. All reports must be "Quant Reviewed" before they can become part of the initial calibration processing method for sample analysis.

- Enter into the "Environmental Data Analysis" (off-line) screen.
- Go to "File" and under method, select the processing method (136Cong0605BNA5.m) that the initial calibration standards will be quantitated with.
- Go into "Quant" and select "QEdit Quant Results" to process the data files. See SOP Manual Integration 08-03 for manual integration details and Section 11.0 for processing of PCB Congener standards.
- When processing is complete for the first standard, "Save" the changes and "Exit." Re-print the re-processed data file by "Generating Quant Report," and save the hard copy for each level of the initial calibration.
- Repeat these steps for all initial calibration standards analyzed within the sequence.
- When the appropriate levels have been processed, go into "IntiCal," and select "Update Levels," and enter all levels for the initial calibration at the proper concentrations. Note: The PCB Homolog group responses *must be hand entered* into the calibration curve, or utilizing the RF macro, (i.e., for Monochlorobiphenyl, Dichlorobiphenyl, etc.) using the response of the appropriate calibration congener (i.e., BZ1, BZ8, etc.).
- After all responses are entered, "Save" the completed method and print the resulting response factor summary by selecting "Response Factors to Printer."
- Acceptance Criteria: 20% RSD for all target compounds, except 10% of the analytes may be >20% RSD but  $\leq$  30% RSD. All calibration standards must be analyzed within 12-18 hours.
- Replace the Qion ratio values from the mid-point concentration level of the ICAL, by checking off the appropriate box, then update and "Save" the new method.
- Replace the reference spectra for the method from the spectra in the mid-point concentration level of the ICAL by going into "ConCal" and select "Update Reference Spectrum." Again, "Save" the method.
- Establish retention time window ranges from the first and last eluting congener within each chlorination level. Set the integration window ranges for each Homolog group



(i.e., Monochlorobiphenyl, Dichlorobiphenyl, etc.) by using the Easy ID function in the Enviroquant software.

**10.2.5** If using greater than five calibration levels in the initial calibration, standards must only be excluded from either extreme. That is, the low-level standard or the high-level standard may be dropped to generate a five-level initial calibration. However, an intermediate-level calibration standard must not be dropped to convert a failing six-level initial calibration curve into a passing five-level initial calibration curve. Reduction in the number of calibration standards must also reduce the linear dynamic range used to quantify analytes in samples. The resulting average response factor for each target analyte in the initial calibration curve will be used by the computer software to calculate actual sample concentrations. See Section 11.0 for additional calculation details.

**10.2.6** The following *corrective actions* are recommended for failing initial calibrations:

- Perform instrument maintenance and repeat the initial calibration, OR,
- Qualify all results reported for the analyte failing in the initial calibration, including all Homolog chlorination range(s) quantified using the suspect average response, and any non-detects. If the failure of the suspect average response appears related to a loss in MS sensitivity, instrument maintenance and repeat of the initial calibration curve must be performed.

The choice of corrective action must be made in consultation with the Section Supervisor, QA Manager, Project Manager, and/or the client. The reasoning for choosing the second option must be documented in the project narrative to the client.

**10.2.7** Alternately, a linear regression model may be employed, provided that the coefficient of determination (COD or  $r^2$ ) is  $\geq 0.99$ . Otherwise, construct a nonlinear calibration of no more than a third order equation. Statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approach. A quadratic (second order) model requires six standards, and a third order polynomial requires seven standards. In setting model parameters, do not force the line through the origin. The COD or  $r^2$  must be greater than or equal to 0.99. The experienced analyst must select the regression order, which introduces the least calibration error into the quantitation.

**10.2.8** Complete the initial calibration by filling out the *Initial Calibration Checklist*. The initial calibration, along with any corresponding continuing calibration data and sample data, is then forwarded for secondary review.

**10.2.9 Initial Calibration Verification - ICV (separate source)**

The analysis of separate source standard must follow the initial calibration curve.

After final processing, calculate the percent recovery of each congener by using the following calculation:

$$\% \text{ Recovery} = \text{Found Amount} / \text{True Value} \times 100$$

Acceptance Criteria: All compounds must agree within +/-30%D.

### 10.3 Equipment Operation and Sample Processing

- 10.3.1** Evaluate the PFTBA tune and/or DFTPP tune as described in Sections 10.1.1 and 10.1.2. *The type of tune required will depend upon the client/project DQOs.*
- 10.3.2** If Pesticides are targets of interest, a PEM must be analyzed and evaluated as mentioned in Quality Control Section 9.7.4.
- 10.3.3** Samples are prioritized for analysis by the Organic Section Supervisor or GC/MS Group Leader based on client due date and sample analytical hold time. Samples are retrieved from the sample storage refrigerator, spiked with 20uL of the chosen internal standard solution per 1mL extract from either Section 8.11 or 8.12, and loaded into the instrument autosampler trays following the generalized sequence below.
- Tune – (5 ug/mL) full scan using DFTPPBNA.m
  - CCV – (50 ng/mL) using 136BNA5.m or PCB209BNA2.m
  - Method Blank – (ID from sample preparation batch)
  - LCS – (ID from sample preparation batch)
  - SRM – (ID from sample preparation batch)
  - Samples (up to 12-18 hours of analytical time)
  - Tune – (5 ug/mL) full scan using DFTPPBNA.m
  - CCV – (50 ng/mL) using 136BNA5.m or PCB209BNA2
  - Samples (up to 12-18 hours of analytical time)
  - CCV – (50 ng/mL) using 136BNA5.m or PCB209BNA2
- 10.3.4** Samples are processed from "Not Reviewed" data files, to "Quant Reviewed" data files in a similar way the standards were previously processed. See Section 11.0 for details on sample processing. If a CCV fails the criteria outlined in Section 10.4.3, all samples since the last acceptable CCV must be re-analyzed.
- 10.3.5** If the on-column concentration of any compound exceeds the concentration of the highest calibration standard, the sample must be diluted, re-spiked with the appropriate amount of internal standard and re-analyzed. Assuming all samples are at a 1mL final volume, the following example dilutions would apply. Adjust the volumes accordingly for other sample final volume amounts and other desired dilutions.
- 1:2 dilution = 500uL of sample : 500uL Hexane and 10uL of IS
  - 1:4 dilution = 250uL of sample : 750uL Hexane and 15uL of IS
  - 1:5 dilution = 200uL of sample : 800uL Hexane and 16uL of IS
  - 1:10 dilution = 100uL of sample : 900uL Hexane and 18uL of IS, etc.



## 10.4 Continuing Calibration

A continuing calibration verification (CCV) standard, at the concentration of the mid-level of the initial calibration curve, must be analyzed at the beginning and end of every analytical sequence, and every 12-18 hours within the sequence, to confirm instrument stability, via response factor, for each calibrated congener.

**10.4.1** After successful analysis of the PFTBA or DFTPP tune (Section 10.1.1 or 10.1.2), "Edit" the "Sample Table Log" to include the 50 ng/mL CCV standard and acquire the CCV against the correct initial calibration method. "Save," then "Load and Run" the sequence, as in Section 10.2.3.

**10.4.2** When the sequence has finished running, the Enviroquant software will generate a "Not Reviewed" quantitation report. All reports must be "Quant Reviewed" against the processing method for sample analysis.

- Enter into the "Environmental Data Analysis" (off-line) screen.
- Go to "File" and under method, select the method that the CCV was analyzed under, then select the CCV data file.
- Go into "Quant" and select "QEdit Quant Results" to process the CCV file. See SOP Manual Integration 08-03 for manual integration details and Section 11.0 for processing of PCB congener standards.

When processing is complete, go into "ConCal," and select "Evaluate Data File as Continuing Calibration." **Note:** The PCB Homolog group CCV responses may be omitted since the calibration congener associated with the Homolog group, is the quantitation congener for that same Homolog group.

**10.4.3** Acceptance Criteria: Compare the CCV resulting response against the average response for the initial calibration for each calibrated congener and/or pesticide, and calculate the % difference (%D). See Section 11.0 for the calculations. The %D for each calibrated congener and/or pesticide must be below 20%D, except up to 20% of the analytes may be > 20%D but ≤ 30%D. If multiple CCVs are analyzed within an analytical sequence, each CCV must be analyzed within 12-18 hours of the previous CCV, and each CCV, including the ending CCV, must meet the acceptance criteria.

Additional Criteria:

- 1) The areas for masses of the internal standards used should not have degraded more than 50% from the previous calibration standard analyzed.
- 2) The retention time of the internal standards must be within 30 seconds of the previous daily standard.

If the CCV meets the acceptance criteria, save the hard copy for each CCV standard and include it with the *Continuing Calibration Checklist*.

Go back into "ConCal" and select "Update Continuing Calibration" and "Save" the method updated to the opening CCV of the day.

**10.4.4** If the CCV does not meet the criteria for each calibrated analyte, the following *corrective actions* are recommended:

- Perform instrument maintenance and re-analyze the continuing calibration standard and all affected samples, OR,
- Perform instrument maintenance and repeat the initial calibration, and re-analyze all affected samples, OR,
- If the closing CCV does not meet the criteria and the sample chromatograms show obvious matrix interference, no re-analysis is necessary. This decision must be made

*with approval of the Section Supervisor.* CCV outliers and affected samples must be noted in the case narrative to the client.

- If the failure of the suspect response appears related to a loss in MS sensitivity or other instrument related issues, instrument maintenance and repeat analysis of all affected samples and/or the initial calibration curve must be performed.

The choice of corrective action must be made in consultation with the Department Manager, QA Manager, Project Manager, and/or the client. The reasoning for choosing the third option must be documented in the project narrative to the client.

## 10.5 Preventive Maintenance

**10.5.1** Preventive maintenance may include the following: replacing glass liner, ferrules, PTV injection port bottom adapter and/or clipping a length of the analytical column.

**10.5.2** Additionally, preventive maintenance for GC-MS system may involve baking out the injection port and the oven, cleaning the ion source, and/or replacing the analytical column.

## 11. Data Evaluation, Calculations and Reporting

**11.1** After sample analysis, "Not Reviewed" quantitation reports are generated by the software system. It is expected that situations will arise when the automated quantitation procedures of the chromatographic software provide inappropriate quantitations or integrations. This normally occurs when there is compound co-elution, baseline noise or matrix interference with the PCB congener compounds. However, with PCB Homolog groups, a range or cluster of peaks is evaluated and manual integration must be performed for each PCB Homolog group or chlorination level cluster.

**11.2** Qualitative identification of multicomponent analytes (Aroclors) requires pattern matching between the calibration standards and the response observed in the sample on both columns. Retention time windows should be used as a gauge; however, pattern recognition for the multicomponent analytes is most important. For samples with PCB Aroclors positively identified, compare the responses of the 3 to 5 major peaks in the single point calibration standard for that Aroclor with the responses of the peaks observed in the sample extract. The relative peaks and number of peaks in the sample should be similar to that observed in the standard; however, degradation, weathering and interferences may cause the sample pattern to differ from that observed in the standard. The peaks chosen for quantitation must be free from interferences. If the interference or co-elution/overlapping with another Aroclor is observed, the analyst has an option to exclude the affected peaks from the final calculation. At least 3 out of 5 peaks must be used to provide the final concentration. Calculate the concentration of each corresponding peak in the sample chromatogram and the 3 to 5 resulting concentrations are averaged to provide the final result for the sample.

**11.3** Identification of the PCB congener and pesticide compounds are based on gas chromatographic relative retention times (RRTs) from the analysis of the mid-level initial calibration standard. For these compounds, manual quantitations are performed, if necessary, by integrating the area of the quantitation ion or peak. For the ten *PCB Homolog groups*, the Homolog groupings (*i.e.*, Dichlorobiphenyl) appear in the extracted ion current profiles (EICPs) as a cluster of congeners with the same degree of chlorination. Establish the pattern of each Homolog group by comparing the primary and secondary ion profiles. Refer to the Manual Integration SOP 08-03 for details on Manual Integration. Manually integrate candidate peaks by straight-line integration to the baseline, taking into account background noise in the EICPs for each Homolog group within each determined Homolog-specific retention time window. If a discrete peak, either target or non-target, does not have a confirmation ion, or the experienced

analyst judges that the confirmation ion does not meet the ratio criteria, the area for that discrete peak can be measured and subtracted from the total area used to calculate the concentration for that Homolog group. The experienced analyst can also choose not to include the interference in the manual integration even if the interference appears within the retention time window established by retention time markers for specific Homolog group. If there is interference observed within Homolog-specific retention time window that cannot be excluded or subtracted out, the results for the affected Homolog group will be qualified with the G flag. See the most recently generated "detailed" PCB reference spectrum hardcopy that is based on the most recent analysis mid-point standard of the ICAL. Table II, in Section 16.0, lists the representative ion(s) used for quantitation and confirmation of each parent congener and PCB Homolog group.

**Note:** Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

**11.4** From EICP of the quantification (primary) mass ions and the confirmatory mass ions, identify all target analytes according to the following criteria:

- Surrogates and internal standards should meet the acceptance criteria in Section 12.0.
- Examine the chromatograms for evidence of saturated ions in mass spectra. Re-analyze the sample(s) at the appropriate dilution(s), see Section 10.3.4, as needed.
- The characteristic ions (primary and secondary) of each pesticide, congener and/or Homolog group of interest should maximize at the same scan, or within one scan of each other.
- The retention time should fall within  $\pm 10$  seconds of the retention time of the authentic target compound or PCB Homolog grouping. **Note:** For PCB Homolog groups, the most intense peak within the group may not have the exact retention time of a calibration congener. Analyst judgement and referral to each Homolog groups' retention time window and group-specific pattern is essential for identification. Apply analyst judgment regarding corrective action, as needed, when these criteria are not met.
- The relative peak height of the quantitation ion compared to the confirmation ion for parent analyte should fall within  $\pm 50$  percent of the relative intensities of these ions in the reference mass spectrum (i.e., the mid-level standard of the initial calibration curve).

**Note:** The relative intensities of the quantitation and confirmation ions may vary widely within a given group of PCB Homologs. Thus, the pattern of each PCB Homolog cluster, and the retention time window for the cluster, will be the primary identification criteria for PCB Homologs. In some instances, a parent congener that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the experienced mass spectrometrist. Supportive data includes the presence of the secondary ion, but ratio value greater than  $\pm 50$  percent of the primary ion, which may be caused by an interference of the secondary ion. See Section 11.6 for interferences.

**11.5** In instances where manual integrations have been performed, they are assigned one of the Manual Integration codes, (Refer to Manual Integration SOP 08-03) and can be found on the raw data provided within the data deliverable package The "detailed" report, displaying the manual integration, including an "m" qualifier(s) next to the modified or manually integrated compound(s), shall be provided to the LIMS for secondary review. These requirements apply to all standards, QC samples, field samples and blanks.



- 11.6** To calculate the **Relative Standard Deviation** (RSD) of all PCB congeners, Homolog groups, and surrogate compounds for the initial calibration, use the formula below. See Section 10.2 for initial calibration acceptance criteria. Additionally, use the initial multi-point calibration to determine **Relative Response Factors** (RRF<sub>i</sub>s) at each concentration level, for each PCB congener. Average the RRF<sub>i</sub>s from the initial multi-point calibration, to generate mean RRF<sub>i</sub>s, for quantification of each PCB congener. Follow the same calculations for each surrogate compound. The RRF<sub>i</sub> for the quantification of each Homolog group is the RRF<sub>i</sub> of the PCB calibration congener assigned to that Homolog group (*i.e.*, Trichlorobiphenyls are quantified using the RRF<sub>i</sub> of the PCB calibration congener BZ29, which is associated with the Trichlorobiphenyl group). The RRF<sub>i</sub>s are based on the internal standard compounds, and are calculated using the formula below. (The relative response factors for the continuing calibration verifications (RRF<sub>c</sub>s) are calculated using the same formula). See Section 16.0, Table II, for the listing of target compounds and their associated internal standards for quantification.

$$\text{RSD} = \text{SD} / \text{mean RRF}_i \times 100$$

where:

SD = Standard deviation between the five points, for that target analyte.

$$\text{RRF}_i = (A_c \times C_{IS}) / (A_{IS} \times C_c)$$

where:

A<sub>c</sub> = Area of the characteristic ion for the standard compound to be measured.

A<sub>IS</sub> = Area of the characteristic ion for the representative internal standard compound.

C<sub>IS</sub> = Concentration of the representative internal standard compound (ng/mL).

C<sub>c</sub> = Concentration of the standard compound to be measured (ng/mL).

**Note:** Assign the response factor of the calibration congener compound to the Homolog group, (*i.e.*, use BZ 5/8 for the Dichlorobiphenyl group).

- 11.7** Based on the mean RRF<sub>i</sub>s, calculate the **Sample Extract Amount** for each Pesticide, PCB congener or Homolog group and surrogate in the sample extracts using the following formula:

$$Q_e = (A_a \times Q_{IS}) / (A_{IS} \times \text{RRF}_i)$$

where:

Q<sub>e</sub> = Sample extract concentration (ng/mL) of target analyte, from quantitation report.

A<sub>a</sub> = Area of the characteristic ion for the target analyte.

A<sub>IS</sub> = Area of the characteristic ion for the representative internal standard compound.

Q<sub>IS</sub> = Concentration (ng/mL) of representative internal standard compound, from quantitation report.

- 11.8** Calculate the **Sample Concentration** (C) for each Pesticide, PCB congener or Homolog group by the following formula:

$$C = (Q_e / V_s) \times FV \times DF$$

where:

C = Concentration in sample (ng/L water, ug/Kg sediment/tissue or ng/cert for PUF).

V<sub>s</sub> = Original volume or weight of sample extracted, corrected for % solids, if applicable. (To correct for % solids, multiply the sample weight by the % solid as expressed as a decimal. For example: 15.24g x 0.843 = 12.85, for a sample size of 15.24g at 84.3% solid).

DF = Dilution factor

FV = Sample Final Volume or Final Effective.

If the response of any analyte in a sample exceeds the linear response range, as defined by the initial calibration standards in Section 10.2, dilute the extract so that the concentration of that analyte falls within the range of the calibration curve.

**Note:** A Homolog group and PCB Aroclor exceeds the calibration level if one single peak in the integration group exceeds the linear response range. If no single peak exceeds the range the total integration range may be above the concentration response range. If the target compound in a sample is detected below the reporting limit (RL) but above half of the RL, qualify the reported concentration with a "J". If any target compound is found in the method blank and in the associated sample(s), qualify the reported concentration with a "B" if detected less than 5x the blank concentration for this analyte.

- 11.9** To calculate **Total PCBs** when analyzing for less than 209 PCB Congeners use the following:

- Each Homolog group will be identified and final concentration will be calculated using the formulas above.
- Sum all Homolog group concentrations.
- If a Homolog group is non-detect, zero is used in the summation. This minimizes the potential for a high bias result.

To calculate **Total PCBs** when analyzing for all 209 PCB Congeners, sum all identified congeners.

- 11.10** Calculate the **Surrogate Recoveries** relative to the internal standards by the following formula:

$$\%R_{sc} = (A_{sc} / A_{is}) \times (Q_{is} / Q_{sc}) \times (100 / RRF_{sc}) \times DF$$

where:

Q<sub>is</sub> = Amount of the representative internal standard (ng).

DF = Dilution factor or fraction of the original extract.



- 11.11** Compare response factors for each PCB congener in the *Continuing Calibration Verification* (CCV), to those of the initial calibration curve by determining the percent difference.

$$\text{Percent Difference (\%D)} = ([RRF_i - RRF_c] / RRF_i) \times 100$$

where:

RRF<sub>i</sub> = Mean response factor from initial calibration.

RRF<sub>c</sub> = Response factor from CCV.

- 11.12** All results must be reported to three significant figures. All solids including soils, sediments, and sludge must be reported on a dry-weight basis. Tissue results may be reported on a dry-weight, or "as received," basis depending upon client request. PUF samples are reported "as received".
- 11.13** The primary analyst does data entry, or upload of the data, into the LIMS system. The LIMS is "linked" to the instrument, so the analyst must choose the sample(s) to be reported from that instrument's analytical sequence. All associated preparation and instrumental QC samples and dilutions are also chosen. Once the data/samples have been selected and "associated" with the proper QC samples, the batched data set is sent to print. In addition to the concentration of each selected PCB congener and Homolog group on the report, the Total PCB concentration is also reported.
- 11.14** The laboratory generates two types of data packages from the LIMS: "Commercial" or "Standard" for routine projects, and "Full Deliverable" or "CLP-like" for fully data validated projects. A Commercial/Standard package consists of sample results and the associated method blank and LCS/LCSD results. A Full Deliverable/CLP-Like package includes all sample results, all preparation and instrumental QC results and the associated supporting raw data. Check the "Report Type" on the project folder to ensure all required deliverables are included. A secondary review is performed on all data.
- 11.15** Procedures for data and record management must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP, 08-01. All records shall be stored in such a manner as to be safe and accessible for at least 10 years.
- 11.16** Notebooks: Laboratory notebooks are designed to accommodate the specific analysis. Instrument printouts are used to document run sequences, and each daily sequence printout is filed in a three-ring notebook. If a sample requires re-analysis or re-extraction for any reason, a notation is made next to the sample entry on the sequence log. Requests for re-extraction are further documented in the "Request for Re-extraction, Re-clean" logbook. At regular intervals the sequence run log is permanently bound, assigned an internal ID number, and filed accordingly. Such files shall be archived so as to remain available for at least 10 years. All laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage Work Instructions*, WI 108-01, and all record keeping and document control practices.
- 11.17** Electronic records: All data files from computers, attached to instruments, shall be backed up daily onto the proper directory on the server. The backups shall be stored so as to be accessible for 10 years. Movement of the data files to the server is the responsibility of the primary analyst. Server backup and storage is the responsibility of the IT department.

**11.18** The percentage breakdown for DDT and Endrin are:

$$\% \text{Breakdown DDT} = \frac{(\text{Area DDD} + \text{Area DDE})}{(\text{Area DDD} + \text{Area DDT} + \text{Area DDE})} \times 100$$

$$\% \text{Breakdown Endrin} = \frac{(\text{Area Endrin Ketone} + \text{Area Endrin Aldehyde})}{(\text{Area Endrin} + \text{Area Endrin Ketone} + \text{Area Endrin Aldehyde})} \times 100$$

## 12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

All PCB congener, Pesticides and Homolog results are reportable without qualification if analytical holding times are met, preservation requirements (including cooler temperatures) are met, and all QC criteria defined in the table below are met. If any of the below QC parameters are not met, all associated samples must be evaluated for re-analysis. See Sections 9.0 and 10.0 for additional QC discussion including corrective actions for any QC outliers.

QC Parameter	Acceptance Criteria
Initial Calibration Curve	20% RSD for all target analytes with exception for 10% of target analytes to be >20%, but ≤ 30%
Independent Check Verification	+/- 30% recovery of the true values
Continuing Calibration Verification	Analyzed every 12-18 hours, 20% D for all target analytes with exception for 20% of target analytes to be >20%, but ≤ 30%
Method Blank	No analyte at or above the reporting limit, The results are qualified with a "B" for any associated sample concentrations that are less than 5x the blank concentration for this analyte.
Laboratory Control Samples (LCS/LCSD)	40-140%; 30% RPD (sporadic marginal failure criteria applies)
Matrix Spike / Matrix Spike Duplicate	Same as for LCS; 30% RPD between the duplicates.
Sample / Sample Duplicate	30% RPD between the duplicates.
Surrogates	50-125%
Internal Standards	50% - 200% of the daily CCV area for the Internal Standards
SRM	40% - 140% recovery

Section 9.0, Quality Control, defines the corrective actions that must be taken in instances where QC outliers exist.

If non-compliant Pesticide, PCB congener or Homolog results are to be reported, the Department Manager, the Laboratory Director, and/or the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may choose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Department Manager performing the secondary review initiates the project



narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

## **13. Method Performance**

### **13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)**

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

### **13.2 Demonstration of Capability Studies**

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

#### **13.2.1 Initial (IDC)**

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

#### **13.2.2 Continuing (DOC)**

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

## **14. Pollution Prevention and Waste Management**

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

## **15. Referenced Documents**

Chemical Hygiene Plan  
SOP/08-05 MDL/LOD/LOQ Generation  
SOP/08-12 IDC/DOC Generation  
G-006 Waste Management and Disposal SOP

## **16. Attachments**

Table I: PCB Homolog Groups  
Table II: PCB Homolog Quantification, Confirmation Ions



**Table I: PCB Homolog Groups**

Compound	Surrogate and IS Reference		Compound	Surrogate and IS Reference
	136Cong	209Cong		
Monochlorobiphenyls	B	A	<u>Surrogate Compounds</u>	
Dichlorobiphenyls	B	A	DBOB	A
Trichlorobiphenyls	B	A	BZ 198	B
Tetrachlorobiphenyls	B	A	<u>Carbon-labeled Surrogates</u>	
Pentachlorobiphenyls	B	A	BZ 19	A
Hexachlorobiphenyls	B	A	BZ 202	B
Heptachlorobiphenyls	B	B		
Octachlorobiphenyls	B	B	<u>Carbon-labeled ISs</u>	
Nonachlorobiphenyls	B	B	BZ 15	A
Decachlorobiphenyl	B	B	BZ180	B

**Note:** Individual congeners may also be reported, as needed, depending upon client/project specific DQOs. Each congener depends on the level of chlorination would use the surrogates and internal standards similar to its chlorination grouping.

**Table II: PCB Homolog Quantification, Confirmation Ions**

Parameter	1 <sup>0</sup> Ion	2 <sup>0</sup> Ion	CASRN	Acceptance Ratio
Monochlorobiphenyls	188	190	27323-18-8	2.5-3.5
Dichlorobiphenyls	222	224	25512-42-9	1.3-1.7
Trichlorobiphenyls	256	258	25323-68-6	0.8-1.2
Tetrachlorobiphenyls	292	290	26914-33-0	1.1-1.5
Pentachlorobiphenyls	326	324	25429-29-2	1.4-1.8
Hexachlorobiphenyls	360	362	26601-64-9	1.0-1.4
Heptachlorobiphenyls	394	396	28655-71-2	0.8-1.2
Octachlorobiphenyls	428	430	31472-83-0	0.8-1.1
Nonachlorobiphenyls	464	466	53742-07-7	1.1-1.5
Decachlorobiphenyl	498	500	2051-24-3	0.9-1.3