

POLYCHLORINATED BIPHENYLS, ORGANOCHLORINE PESTICIDES, DIOXINS AND FURANS IN BALD EAGLE EGG AND BLOOD SAMPLES FROM THE HUDSON RIVER, NEW YORK

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HUDSON RIVER NATURAL RESOURCE DAMAGE ASSESSMENT

HUDSON RIVER NATURAL RESOURCE TRUSTEES

STATE OF NEW YORK

U.S. DEPARTMENT OF COMMERCE

U.S. DEPARTMENT OF THE INTERIOR

FINAL

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EXECUTIVE SUMMARY

Past and continuing discharges of polychlorinated biphenyls (PCBs) have contaminated the natural resources of the Hudson River. The Hudson River Natural Resource Trustees – New York State, the U.S. Department of Commerce, and the U.S. Department of the Interior – are conducting a natural resource damage assessment (NRDA) to assess and restore those natural resources injured by PCBs.

The Hudson River supports a rich array of ecological resources that interact in complex ways, and provides habitat for a wide range of plants and animals. As part of the NRDA, the Trustees are documenting exposure of the natural resources of the Hudson River to PCBs.

One of the species for which the Hudson River provides habitat, and which has been exposed to PCBs, is the bald eagle (*Haliaeetus leucocephalus*). Bald eagles are at risk of accumulating PCBs because they are at the top of the food web. Eagles prey on fish and scavenge carcasses of birds, mink, otter, and other organisms that may contain PCBs. Because much of the eagles' diet may contain PCBs, they are at risk of accumulating concentrations that are associated with adverse health impacts.

In the 1990s, the Trustees began monitoring Hudson River bald eagle nests for reproductive success. As part of those studies the Trustees collected samples from bald eagles for contaminants analysis.

This report addresses bald eagle egg and blood samples collected from New York in 2003-2004 and analyzed by the U.S. Geological Survey, Biological Resources Division, Columbia Environmental Research Center in Columbia, Missouri.

Specifically this report provides the analytical results for seven bald eagle blood samples (including two from the Hudson River¹) and eighteen bald eagle egg samples (including six from the Hudson River²) which were analyzed for total PCBs and selected congeners, organochlorine pesticides, non-ortho substituted PCB congeners, and dibenzo-p-dioxins and dibenzofurans.

Within this complete set of samples, total PCB concentration in the bald eagle blood samples ranged from 42 ppb to 520 ppb, and total PCB concentration in the bald eagle egg samples ranged from 3,300 ppb to 120,000 ppb ww. Note that these units are not fresh wet weight.

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1. Blood samples with Field IDs 1264 and 1321 from Astor Cove and Waterford, respectively.
 2. Egg samples from Cruger's Island, Gay's Point, Castleton Island, Rogers Island (Columbia County), Inbocht Bay, and Bronx Island.



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Dioxins and Furans in Bald Eagle Egg and Blood Samples
from the Hudson River, NY**

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I. Project Background and Summary

The Hudson River is highly contaminated with polychlorinated biphenyls (PCBs) from industrial sources, primarily, two capacitor manufacturing facilities operated by General Electric. The 200 river miles from the New York Harbor upstream to Hudson Falls, New York, are designated a Superfund Site. From 1946 until 1977, an estimated 209,000 to 1.3 million pounds of PCBs were discharged into the waters of the Hudson River by these two plants (1). The Ft. Edward Dam retarded downstream movement of the PCBs until its removal in 1973, at which time the heavily contaminated sediments and detritus began to migrate downstream. In addition to contamination of the river itself, dredging operations have deposited contaminated material at nine known upland sites adjacent to the river.

Contamination of water, sediments, and fish along the Hudson River by PCBs has been examined, but less is known about the concentration and movement of the contaminants among other trophic levels. Many resident and migrating avian species may be affected, including a fairly substantial population of wintering bald eagles (*Haliaeetus leucocephalus*).

The contaminant residue information provided in this report is part of a larger study concerned with assessing eagle reproductive health in PCB contaminated regions of the Hudson River valley. While PCBs are the predominate contaminates of concern, this report also addresses other persistent organic pollutants (organochlorine pesticides, dibenzo-*p*-dioxins and dibenzofurans) that may contribute to reproductive health issues of bald eagles. Reported are the results of the analyses of the following contaminants in the eagle egg and blood samples:

Congener specific polychlorinated biphenyls (c-PCBs),
Non-*ortho* PCBs (n-PCBs),
Persistent organochlorine pesticides (OCPs), and
Dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs).

II. Sample Collection

Samples were collected by the NY State Department of Environmental Conservation and shipped under chain of custody from Peter Nye to the Columbia Environmental Research Center (CERC). Samples were verified against the chain of custody documentation, entered into the CERC database, given unique database numbers, and kept frozen (-18 to -20°C) prior to analysis.

II. Summary of Analytical Methods

1. Sample Preparation

Eagle egg and blood samples were analyzed for residues of selected congeners of PCBs (c-PCBs), non-*ortho*-chlorinated PCBs (n-PCBs), organochlorine pesticides (OCPs), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) according to the procedures outlined in Figure 1. Triplicate egg samples were analyzed

with each set to determine method reproducibility. The following quality control (QC) samples were incorporated into the various analyses:

- Procedural blanks
- Chicken egg matrix blanks (for the egg analyses)
- Chicken egg matrix spikes (PCBs, OCPs, and PCDDs/PCDFs spiked for egg analyses)
- Bovine serum matrix blanks (for blood analyses)
- Bovine serum matrix spikes (PCBs, OCPs, and PCDDs/PCDFs spiked for blood analyses)

The matrix QC samples (blanks and spikes), prepared from clean chicken egg or bovine serum, were analyzed with each set of samples. At least one of each category listed above was analyzed with each set of samples.

All samples, including QC samples, had method recovery compounds added to them before extraction to monitor recoveries throughout the cleanup procedures. The following compounds were added to all samples:

- PCB-29 (2,4,5-trichlorobiphenyl)
- PCB-155 (2,2',4,4',6,6'-hexachlorobiphenyl)
- PCB-204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl)
- d_8 -labeled p,p'-DDD
- Four ^{13}C -labeled non-*ortho*-PCB congeners (PCB-77, PCB-81, PCB-126 and PCB-169)
- 14 ^{13}C -labeled 2,3,7,8-substituted PCDDs/PCDFs.

To evaluate the c-PCB and n-PCB method recoveries, blank matrix was spiked at 2 $\mu\text{g/g}$ with a mixed Aroclor standard prepared from commercial Aroclor mixtures of 1242, 1248, 1254, and 1260. This mixture contained native (^{12}C) n-PCBs at levels in the Aroclors ranging from 1,300 ppm for PCB-77 to <7 ppm for PCB-169. Final concentrations in the matrix spike ranged from 2,600 pg/g PCB-77 to <14 pg/g PCB-169. To evaluate PCDD/PCDF method recoveries, blank matrix was spiked with native (^{12}C) PCDDs and PCDFs at levels from 400 pg/g to 40 pg/g of each 2,3,7,8-substituted congener (refer to Tables 9 and 11).

To evaluate the OCP method recoveries, separate blank matrices were spiked at 40 ng/g with an OCP standard mixture, obtained commercially (AccuStandard, New Haven, CT), containing 29 individual OCPs.

For the analytical procedures, egg and blood samples were dehydrated by addition of anhydrous sodium sulfate, and method recovery compounds were added. The exact mass of sample analyzed is reported in the attached data tables. Samples were column-extracted with dichloromethane, and a small portion of the extract (2%) was used to determine percent lipid (2, 3). Lipids and co-extracted biogenic materials were removed using low pressure size exclusion chromatography (LP-SEC) (4) followed by high performance size exclusion chromatography (HP-SEC) (5). The extracts were then fractionated on two-layered octadecylsilica (ODS)/activated silica gel 60 columns into

two fractions (6): SODS-1 containing PCBs, five targeted OCPs, PCDDs and PCDFs, and SODS-2 containing some of the less-chlorinated PCBs and the remaining OCPs which were analyzed by dual column gas chromatography/electron capture detection (GC/ECD). The SODS-1 fraction was further fractionated on high pressure porous graphitic carbon (HP-PGC) (7) into the following PGC fractions:

- PGC-1: *ortho*-chlorinated PCB congeners and five OCPs; analyzed by dual column GC/ECD.
- PGC-2: non-*ortho*-chlorinated PCBs; analyzed by gas chromatography/high-resolution mass spectrometry (GC/HRMS).
- PGC-3: PCDDs/PCDFs; analyzed by GC/HRMS following alumina enrichment.

The PGC-3 fractions were further enriched using low pressure basic alumina column chromatography (8) to remove non-polar biogenic materials, polychlorinated naphthalenes, polychlorinated diphenyl ethers, and residual PCB congeners.

2. Summary of gas chromatographic method for PCB congeners

The final volumes of the sample extracts were adjusted to provide approximate 1 µg/mL solutions. Two instrumental internal standards (PCB-30 (2,4,6-trichlorobiphenyl) and PCB-207 (2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl)) were added to each extract at 40 ng/mL. Individual PCB congeners were measured in the PGC-1 and SODS-2 fractions by GC/ECD. Analyses were performed using Hewlett-Packard 5890 Series II GCs with cool on-column capillary injection systems and Hewlett-Packard model 7673 autosamplers (9). For all analyses, 3 m sections of 0.53 mm i.d. uncoated and deactivated capillary retention gap (Agilent, Palo Alto, CA) were attached to each analytical column by Press-Tight® (Restek Corp., Bellefonte, PA) unions. The analytical columns were 60 m x 0.25 mm x 0.25 µm DB-5 (5% phenyl-, 95% methylsilicone, Agilent, Palo Alto, CA) and DB-17 (50% phenyl-, 50% methylsilicone, Agilent, Palo Alto, CA). The H₂-carrier gas was pressure regulated at 25 psi. The temperature program for the PCB analysis was: initial temperature 60°C, immediately ramped to 150°C at 15°C/min, then ramped to 260°C at 1°C/min, and finally ramped to 300°C at 10°C/min, and held for 15 min. The electron capture detector temperature was 330°C with nitrogen as the makeup gas at a flow rate of 25 mL/min.

PCB congeners were matched and identified on one or both GC capillary columns with known PCB peaks from the mixed Aroclor standards. Capillary GC/ECD data were collected, archived in digital form, and processed using a PerkinElmer chromatography data system, which included the model 970 interface and version 6.2 of TotalChrom Workstation chromatography software, on a Pentium III microcomputer (9, 10). A 1:1:1:1 mixture of Aroclors 1242, 1248, 1254 and 1260 was used to produce the PCB congener calibration standards. These standards have been quantified based on pure primary PCB standards (Accustandard, New Haven, CT) and were used as secondary calibration standards (11). Up to five levels of calibration for each individual congener were used to quantify approximately 140 congeners in the samples. In terms of total PCB concentrations, the calibration curve covered a range of 50 to 8,000 ng/mL.

The method detection limits (MDLs) for individual PCB congeners and for total PCBs were based on procedural blank (PB) results following the method outlined by Keith *et al.* (12, 13). Briefly, a mean (\bar{x}_{PB}) and standard deviation (SD) were determined using PB results from the past several years for a better statistical sample ($n > 10$) (14). This produced a long-term MDL (ng) calculated using the following formula:

$$MDL = \bar{x}_{PB} + 3(SD_{PB})$$

The MDL was then expressed in units of concentration, e.g. mass of analyte per mass of sample. The long term MDL was divided by the average mass of the samples analyzed in the same period of time used to calculate the \bar{x}_{PB} .

The method quantitation limits (MQLs) for congeners was calculated in the same manner as above using the following formula:

$$MQL = \bar{x}_{PB} + 10(SD_{PB})$$

Recoveries of analytes were monitored by measuring the procedural internal standards spiked into each sample, and the 1:1:1:1 Aroclor mixture spiked into chicken egg or bovine serum analyzed with each set.

Three procedural standards were used to correct for analytical recoveries of the PCBs: PCB-29, a trichlorobiphenyl, is representative of more volatile early eluting PCBs ($Cl_1 - Cl_3$); PCB-155, a hexachlorobiphenyl, is representative of mid-range eluting congeners ($Cl_4 - Cl_6$); and PCB-204, an octachlorobiphenyl, is less volatile and representative of later eluting PCBs ($Cl_7 - Cl_{10}$).

3. Summary of gas chromatographic method for OC pesticides

The final volumes of the sample extracts were adjusted to provide approximate 1 $\mu\text{g}/\text{mL}$ solutions. Two instrumental internal standards (PCB-30 and PCB-207) were added to each extract at 40 ng/mL . Individual organochlorine pesticides were measured in both the PGC-1 and SODS-2 fractions by GC/ECD. Analyses were performed using Hewlett-Packard 5890 Series II GCs with cool on-column capillary injection systems and Hewlett-Packard model 7673 autosamplers (15). For all analyses, 3 m sections of 0.53 mm i.d. uncoated and deactivated capillary retention gap (Agilent, Palo Alto, CA) were attached to each analytical column by Press-Tight® (Restek Corp., Bellefonte, PA) unions. The analytical columns were 60 m x 0.25 mm x 0.25 μm DB-5 and DB-17 columns (Agilent, Palo Alto, CA). The H_2 -carrier gas was pressure regulated at 25 psi. The temperature program for the OCP analysis was: initial temperature 60°C, immediately ramped to 150°C at 15°C/min, then ramped to 260°C at 1°C/min, and finally ramped to 300°C at 10°C/min, and held for 15 min. The electron capture detector temperature was 330°C with nitrogen as the makeup gas at a flow rate of 25 mL/min .

The dual column method accurately identifies and quantifies OCP peaks from both columns, as a peak identification confirmatory method, based upon known standards. The GC/ECD data were collected, archived in digital form, and processed using a

PerkinElmer chromatography data system, which included the model 970 interface and version 6.2 of TotalChrom Workstation chromatography software, on a Pentium III microcomputer (10, 15). Six levels of OC pesticide standards (29 components) were used for calibration, with each pesticide at concentrations ranging from 0.1 to 80 ng/mL.

Recoveries of analytes were monitored by measuring procedural internal standards spiked into each sample, and OCPs spiked into chicken egg or bovine serum analyzed with each set.

Three method recovery compounds were used to account for analytical recoveries of the OCPs: PCB-29, a trichlorobiphenyl, is split between the SODS-1 and SODS-2 fractions and is representative OCPs which are also split between the two fractions; PCB-155, a hexachlorobiphenyl, is contained in the SODS-1 fraction and is representative of the OCPs that elute in this fraction; and d_8 -labeled p,p'-DDD which elutes in the SODS-2 fraction and is representative of the OCPs in this fraction. The matrix samples spiked with OCPs were also used to evaluate recoveries.

4. Summary of GC/HRMS method for non-*ortho*-PCBs

A total of 5 ng of instrumental internal standard (^{13}C -labeled 2,2',4,5,5'-PeCB, PCB 101) was added to each non-*ortho*-PCB fraction (PGC-2) previously adjusted to a final volume of 100-150 μL . The non-*ortho*-PCBs were determined by GC/HRMS, monitoring two sequential mass windows during the chromatographic separation (16, 17). GC/HRMS analysis was performed with a HP 5890A capillary gas chromatograph interfaced to a VG 70S high-resolution mass spectrometer and OPUS Alpha data system. An HP 7673 autosampler was used to inject 5 μL of the final extract into a 1.7 m x 250 μm Siltek-deactivated fused silica retention gap via heated (275°C) direct on-column injection with a Restek Siltek-deactivated spiral Uniliner. The analytical column was a narrow bore, thin film Solgel-1MS capillary column (40 m x 180 μm x 0.1 μm , SGE, Austin, TX). The GC oven was held at 150°C for 1 min, programmed to 210°C at 2°C/min, then ramped to 310°C at 4°C/min with no final hold. Helium carrier gas was maintained at 60 psig with an initial linear velocity of 30 cm/s.

The GC/HRMS system was tuned to a resolution of 10,000 and calibrated using perfluoro-tetradecahydro-phenanthrene. Non-*ortho*-PCBs were analyzed by selected ion monitoring of two sequential groups. Group 1, from 11-35 min, included ions for tetrachlorobiphenyls 77 and 81, pentachlorobiphenyl 126, and corresponding ^{13}C -surrogates; Group 2, from 35-56 min, included ions for hexachlorobiphenyl 169 and its ^{13}C -surrogate. Within each mass window, the two most abundant ions were measured for positive identification and quantitation of each analyte. The ion responses were quantified and averaged. Within each mass window, additional ions were monitored to verify successful PGC fractionation. The additional compounds monitored included: potential-interfering PCB congeners, tetra- and pentachloro-terphenyls (PCTs), hexabromobiphenyls, tetra-, pentabromo- and hexachloro-diphenyl ethers, tetra-through octachloro-naphthalenes (PCNs), TCDF, and hexachloro-dibenzothiophenes (Hx-PCDTs).

A calibration curve describing the response of each native congener (0.05 to 2,500 pg/ μ L) to that of its ^{13}C -labeled surrogate (50 pg/ μ L) was used. Quantification is inherently corrected for analytical losses during isolation procedures and variations in the instrumental analysis by the ^{13}C -isotopically labeled surrogates.

Molecular ion responses of residual PCB congeners were measured to ensure that any fragment ion response does not contribute an interference >10% to any response of the respective non-*ortho*-PCB. Column performance was verified by analyzing standards of individual congeners, labeled congeners, and congeners from Aroclor spiked mixtures. Because non-*ortho*-pentachloro-PCB 126 was only slightly resolved from the di-*ortho*-hexachloro-PCB 129, PCB-129's molecular ion response were monitored to assure that its fragment ion response (3.5% abundance) did not contribute an interference of >10% to the response of PCB-126. Thus, the molecular ion response of the residual PCB-129 must not exceed three times that of PCB-126. Adequate mass resolution (> 4000) was verified by monitoring ions of tetrachloro- through octachloro-PCNs to ensure no interference occurred with ions of the ^{13}C -labeled PCBs.

Criteria for Confirmation: For the positive identification and quantitation of each congener, the following criteria were established and met in this study:

1. Peak areas for the selected ion responses must be greater than three times background noise. If not, an "ND" (not detected) flag with a detection limit is entered into the concentration results table.
2. Native ion peaks must occur at retention times from -1 to +3 sec that for the corresponding ^{13}C -labeled ion peaks, that elute about 1 sec earlier.
3. The ion ratio for the two principal ion responses must be within the acceptable range ($\pm 15\%$). If not, a "LQ" (less than quantitation limit) flag is entered into the concentration results table to qualify the result.

A known amount of the internal standard mixture was spiked into the final extract and used to calculate the amounts of the surrogate recovered in the final extract. The efficiency of the extraction and cleanup was measured by comparing the quantity of the surrogates detected in the final isolated extract (at GC/HRMS analysis) with the quantity spiked into the sample at the beginning of the extraction step.

5. Summary of GC/HRMS method for dioxins and furans

A total of 1 ng each of the internal standards, ^{13}C -labeled 1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD, was added to each PCDD/PCDF fraction (PGC-3) previously concentrated to a volume of about 35 μ L. PCDFs and PCDDs were determined by GC/HRMS by monitoring five sequential mass windows of selected ions during the chromatographic separation (18). GC/HRMS analysis was performed using an Agilent 6890N capillary gas chromatograph interfaced to a Waters Autospec high-resolution mass spectrometer. An HP 7683 autosampler was used to inject 1 μ L of the extract from a conical vial directly into the 1.7 m x 530 μ m deactivated fused silica retention gap via a cool on column injector. The analytes of interest were separated on a BPX5 capillary column (40 m x 180 μ m x 0.1 μ m, SGE, Austin, TX). The GC oven was held for 1 min at 155°C followed by a ramp to 190°C at 10°C/min, then to 265°C at 1.8°C/min, and a final

ramp to 300°C at 3°C/min. The helium carrier gas was maintained at a constant flow of 1 mL/min with an initial linear velocity of 30 cm/s.

The GC/HRMS system was tuned to 10,000 R.P. and calibrated using perfluoro-tetradecahydro-phenanthrene. Tetra- through octa-PCDFs and PCDDs were analyzed by selected ion monitoring of five sequential ion groups. Retention times for switching ion groups were established using a window-defining PCDF/PCDD standard mixture and a mixture of PCDTs. Within each mass window, the two most abundant ions were measured for positive identification and quantitation of each analyte. The ion responses were quantified and averaged. Within each mass window, additional ions monitored any responses from potentially interfering penta- through nona-PCDEs, hexa-PCNs, and tri- through octa-dibenzothiophenes (PCDTs).

A calibration curve describing the response of each native congener (0.05 to 2,500 pg/μL) to that of its ¹³C-labeled surrogate (50 pg/μL) was used. Quantification is inherently corrected for analytical losses during isolation procedures and variations in the instrumental analysis by the ¹³C-isotopically labeled surrogates. The calibration curve describing the response of each native congener to that of its labeled surrogate congener was used directly in the calculations. For more accurate low values, each native analyte calibration curve had a quadratic fit with 1/X weighting and excluding the origin. Calibration curves of the ¹³C-surrogates to that of a ¹³C-internal standard were determined using an average response factor.

The thin film, narrow bore column was selected and chromatographic conditions were optimized to resolve 2,3,7,8-TCDD from 1,2,3,7- and 1,2,3,8-TCDD (and from 1,2,3,4-TCDD) by a resolution factor of at least 0.5, which corresponds to a peak overlap of <25%. Column performance was verified by analyzing standards of individual components, and observing the chromatographic resolution of the TCDDs, HxCDDs, and HxCDFs. Similarly, relative retention times for all other congeners of interest were evaluated with respect to labeled analogs.

Adequate mass resolution was verified while monitoring ions for hexa-PCNs vs. ion responses of ¹³C-TCDDs and of native TCDD vs. ¹³C-TCDF throughout the sample set. The latter two ions, both at nominal m/z 320, differ by 0.04 Da, requiring a resolving power of at least 8,000 for nearly complete resolution. Monitoring these ion ratios thereby assures a continual check on mass resolution. For each mass window, lock-mass and lock-mass-check ions were used to maintain and verify the accuracy of mass measurement.

Criteria for Confirmation: For the positive identification and quantitation of a particular congener, the following criteria had to be met:

1. The peak areas for the selected ion responses must each be greater than three times the background noise (S/N >3). If not, an "ND" (not detected) flag with a detection limit is entered into the concentration results table.
2. For congeners with isotopically-labeled analogs, the ion peaks for the native must occur at retention times from -1 to +3 sec that for the corresponding ¹³C-labeled ion peaks, which elute about 1 sec earlier than the native ion peaks;

3. For OCDF (without an isotopically-labeled analog), ion responses in sample analyses must occur at relative retention times (RRTs) from -0.2 to 0.5% of ¹³C-labeled OCDD, analogous to the window above;
4. For the two principal ion responses, the ion ratio must be within the acceptable range (generally $\pm 15\%$). If not, a "LQ" (less than quantitation limit) flag is entered into the concentration results table to qualify the result.

A known amount of the internal standards was spiked into the final extract and used to calculate the amounts of the surrogate recovered in the final extract. The efficiency of the extraction and cleanup was measured by comparing the quantity of the surrogates detected in the final isolated extract (at GC/HRMS analysis) with the quantity spiked into the sample at the beginning of the extraction step.

III. Results and Discussion

1. PCB Congeners

The PCB congener concentrations determined for eagle egg samples and associated QC samples are presented in Table 1. The total PCB concentrations, as a sum of all congeners, are also presented in Table 1. The concentrations of total PCBs in the eagle egg samples ranged from 120,000 ng/g (120 $\mu\text{g/g}$ or ppm) in the 1310-a Castleton Island Nest sample (33275) to 3,300 ng/g (3.3 $\mu\text{g/g}$) in the 1256-c Franklington Vlai., Schoharie, Co. sample (33270). Recovery data for the eagle egg procedural recovery standards are presented in Table 2. Recoveries and precision fell within quality control limits (50% - 125%) with average recoveries for PCB-29, PCB-155, and PCB-204 of 85%, 79% and 77%, respectively. Total PCBs in the method triplicates averaged 9% percent relative standard deviations (%RSD).

The PCB congener concentrations determined for eagle blood samples and associated QC samples are presented in Table 3. The total PCB concentrations, as a sum of all selected congeners, are also presented in Table 3. The concentrations of total PCBs in the eagle blood samples ranged from 520 ng/g (ppb) in the 1321 New Waterford Nest blood sample (33283) to 42 ng/g in the 1317 Montezuma 1 Nest blood sample (33285). Recovery data for the eagle blood procedural recovery standards are presented in Table 4. Recoveries and precision fell within quality control limits (50% - 125%) with average recoveries for PCB-29, PCB-155, and PCB-204 of 79%, 73% and 76%, respectively. Due to the small amount of eagle blood matrix received, triplicate analyses were not performed for the blood samples.

Congener-PCB concentrations determined for eagle egg and blood samples have been corrected for analytical recovery, as monitored by the method recovery compounds. PCB-29 was used to correct the most volatile PCB-1 through PCB-35 congener data, PCB-155 was used to correct the moderately volatile PCB-37/59 through PCB-167 congener data, and PCB-204 was used to correct the least volatile PCB-170 through PCB-209 congener data. The QC sample concentrations were not corrected for method recovery compound recoveries.

Background levels of PCBs in the matrix blanks were 10 to 11 ng/g total PCBs, while the procedural blanks ranged from 10 to 11 ng/g total PCBs. Matrix spike recoveries were in the acceptable QC range (50-125%) with a few exceptions for congeners near the detection limits. The method detection limit for total PCBs was 19 ng/g.

2. Organochlorine Pesticides

The results for analysis of the eagle egg organochlorine pesticides (OCPs) are presented in Table 5. The OCPs detected in the egg samples include:

<u>OCP ID</u>	<u>Range (ng/g)</u>
p,p'-DDE	9,100 to 500
mirex	810 to 11
trans-nonachlor	500 to 62
p,p'-DDD	500 to 12
cis-chlordane	340 to 14
dieldrin	190 to 19
cis-nonachlor	170 to 25
oxychlordane	67 to 10
heptachlor epoxide	24 to <MDL
hexachlorobenzene	14 to 2.2
o,p'-DDE	13 to <MDL
o,p'-DDT	13 to <MDL
trans-chlordane	12 to 0.68
endrin	11 to <MDL
o,p'-DDD	6.5 to <MDL
pentachlorobenzene	6.1 to 0.13
pentachloroanisole	5.7 to 0.21
p,p'-DDT	3.7 to <MDL
b-BHC	3.2 to <MDL
lindane	2.4 to <MDL
heptachlor	2.3 to <MDL
endosulfan II	1.6 to <MDL
endosulfate	1.2 to <MDL
d-BHC	0.22 to <MDL

Aldrin, dacthal, endosulfan I and methoxychlor were not detected or <MDL.

The 1310-a Castleton Island Nest egg sample (33275) and the 1256-c Franklington Vlai., Schoharie, Co. egg sample (33270) showed the highest and lowest total OCP levels, respectively.

The method recovery compound recoveries are presented in Table 6 for the egg samples. Recoveries and precision fell within quality control limits (50% - 125%) with average recoveries for PCB-29, PCB-155, and d₈-labeled p,p'-DDD of 85%, 72% and 90%, respectively.

The results for analysis of the eagle blood organochlorine pesticides (OCPs) are presented in Table 7. The OCPs detected in the blood samples include:

<u>OCP ID</u>	<u>Range (ng/g)</u>
p,p'-DDE	17 to 3.7
p,p'-DDD	3.7 to 0.64
mirex	3.6 to <MDL
endosulfan II	3.3 to <MDL
trans-nonachlor	1.6 to 0.40
dieldrin	1.3 to 0.28
cis-nonachlor	0.83 to <MDL
endosulfate	0.60 to <MDL
p,p'-DDT	0.58 to <MDL
oxychlordane	0.42 to <MDL
dacthal	0.40 to <MDL
hexachlorobenzene	0.36 to <MDL
b-BHC	0.35 to <MDL
heptachlor epoxide	0.28 to 0.08
cis-chlordane	0.28 to <MDL
trans-chlordane	0.27 to <MDL
pentachloroanisole	0.21 to <MDL
o,p'-DDE	0.10 to <MDL
pentachlorobenzene	0.08 to <MDL

Lindane, a-BHC, d-BHC, heptachlor, aldrin, endrin, o,p'-DDD, o,p'-DDT, endosulfan I and methoxychlor were not detected or <MDL.

The 1264 Astor Cove blood sample (33280) and the 1319 Tusten Nest blood sample (33286) showed the highest and lowest total OCP levels, respectively.

The method recovery compound recoveries are presented in Table 8 for the blood samples. Recoveries and precision fell within quality control limits (50% - 125%) with average recoveries for PCB-29, PCB-155, and d₈-labeled p,p'-DDE of 80%, 77% and 92%, respectively.

Concentrations have been corrected for analytical recovery, as monitored by the method recovery compounds. Compounds present in the PGC-1 fraction (pentachlorobenzene, hexachlorobenzene, aldrin, and mirex) are corrected using PCB-155, which is also present in the PGC-1 fraction. Compounds which are split between the PGC-1 and SODS-2 fractions (heptachlor and p,p'-DDE) are corrected using PCB-29, which is also split between these two fractions. The remaining OCPs, (fraction SODS-2), are corrected using d₈-labeled p,p'-DDD, which is also contained in the SODS-2 fraction. The QC sample concentrations were not corrected for method recovery compound recoveries.

Matrix spikes showed poor recoveries for pentachlorobenzene (42% set #1, 38% set #2, and 42% set #3), hexachlorobenzene (49% set #2 and 46% set #3), d-BHC (20% set #1 and 17% set #2), and heptachlor (47% set #1 and 38% set #3). All other recoveries

recoveries were within acceptable QC limits (50% - 125%). Procedural blanks and MDLs were within acceptable QC limits (Tables 5 and 7).

3. Non-*ortho*-PCB Congeners

The concentrations (pg/g, or parts per trillion (ppt)) of non-*ortho*-PCBs (81, 77, 126, and 169) in the eagle eggs and bloods are presented in the bottom of Tables 9 and 11, respectively. In some egg samples, concentrations of PCBs 77, 81, and 126 are comparable, each often exceeding 1,000 pg/g, but in the blood samples, PCB-77 is always predominant, similarly to that in most Aroclors. In eagle eggs, concentrations of PCB-81 vary the most, ranging from 6,240 pg/g (1310-a Castleton Island, 33275) to 48 pg/g (1256-c Franklington, 33270). In birds, PCB-81 has a TCDD-equivalence factor of 0.1, similar to PCB-126 and thus is an important analyte. Along with PCB-81, PCBs 77 and 126 are also both highest in the Castleton Island egg sample (10,400 and 8,400 pg/g, respectively). Together with PCB-81, these non-*ortho*-PCBs contribute the bulk of the total dioxin equivalents in that sample.

Quality control results were within QC guidelines (25 - 125%). PGC fractionation was successful and PCB-129 did not contribute any significant interference (>10%) to the PCB-126 values. Ion ratios for the four non-*ortho*-PCBs in the egg samples are all within the expected QC tolerance ($\pm 15\%$) except for PCB-169 in sample 33273 Replicate 1 which is flagged as "LQ" from an interference with the m/z 360 ion. For all other samples, both blood and QC, the only analyte values that are flagged "LQ", because of incorrect ion ratios, are all very low (≤ 2.3 pg/g) as would be expected. Surrogate recoveries in eagle eggs and bloods, listed in Tables 10 and 12, respectively, are typically above 50%. Non-*ortho*-PCBs in the matrix spike and positive control carp from Saginaw Bay are within 15 – 20% of the historic averages. Concentrations of each non-*ortho*-PCB in all procedural blanks were low (<1 pg/g and <6 pg/g for PCB-77). Concentrations in the bovine serum matrix blank are the same as those in the corresponding procedure blank. Concentrations in both chicken egg matrix blanks were <8 pg/g and less than four times those in the corresponding procedure blanks. Triplicate egg samples showed excellent precision, typically <15%.

4. Dioxins and Furans

Concentrations (pg/g) of 2,3,7,8-substituted PCDDs and PCDFs (pg/g) in bald eagle eggs and bloods are presented in the top part of Tables 9 and 11, respectively. In the egg samples, most PCDFs are low (<3 pg/g), except for 2,3,4,7,8-PeCDF, which ranges from 36 to 2 pg/g in the 1310-a Castleton Island, (33275). Several PCDDs are prominent in the egg samples: 2,3,7,8-TCDD ranges from 22 to 1 pg/g in the 1311 Bronx Island, (33277), 1,2,3,6,7,8-HxCDD from 21 to 3 pg/g in the 1310-a Castleton Island, (33275), and OCDD from 138 to 3 pg/g in the 1246 Gay's Pt, (33263). However, 1,2,3,4,6,7,8-HpCDD remains low in all egg samples, ranging from 5 to 0.4 pg/g. Also detected in some egg samples are several polychlorinated dibenzothiophenes, which have been previously detected in samples from the New York Harbor area. In the blood samples, almost all analytes are <1 pg/g, though 2,3,7,8-TCDF ranged from 2 to 0.2 pg/g and OCDD 6 to 0.7 pg/g.

Quality control results are generally within guidelines with the exceptions discussed below. Percent recoveries of ¹³C-labeled PCDDs and PCDFs spiked into the egg and blood samples, presented in Tables 10 and 12, respectively, are all within our quality assurance range (25 - 125%), except for no recovery of most surrogates in the 1315 Roundout 3 (33279) sample, likely due to failure at the alumina fractionation step. The only surrogates which were partially recovered in sample 33279 all elute earliest from alumina and can be partially eluted with the first solvent eluant of the method. We presume that the other, more retentive surrogates were retained on the alumina column for that sample. Ion ratios for the PCDD/PCDFs in the egg and blood samples are mostly within the expected QC tolerance ($\pm 15\%$); the few exceptions all have very low analyte concentrations (≤ 1.1 pg/g) and are flagged "LQ" in Tables 10 and 12. Three egg samples were processed in triplicate to evaluate method variations. Replicate concentrations are very precise, typically $< 15\%$. 2,3,7,8-PCDDs/PCDFs in QC blank samples are < 1 pg/g, except for OCDF (< 3 pg/g) in both procedural blanks with the egg sets. In both chicken egg matrix blanks, all analytes are also < 1 pg/g except for OCDF and OCDD (< 6 pg/g). Concentrations of all analytes in both chicken egg matrix spikes and the bovine serum matrix spike are with 20% of the analytes' respective concentrations. Finally, concentrations of all analytes in both positive control carp samples from Saginaw Bay are within 15 - 20% of historical averages.

5. Toxic Equivalents

In Table 13, 2,3,7,8-TCDD toxic equivalency factors (TEFs) for birds were used to calculate the total toxic equivalents (TEQs) from mono- and non-*ortho*-PCBs and PCDD/PCDFs in the eagle eggs and bloods (20). Total TEQs in the egg samples ranged from 2,500 to 70 pg/g. In the eagle egg samples, dioxin-like PCBs contributed over 90% of the TEQs. Over 75% of the TEQs result from three non-*ortho* PCBs (77, 81, and 126); dioxin-like mono-*ortho*-PCBs contribute an additional 15%.

For eagle blood samples, listed at the bottom of Table 13, total TEQs ranged from 27 to 2 pg/g. For reference, total TEQs in our QC bovine serum matrix blank are 1 pg/g. In most blood samples, dioxin-like PCBs also contributed the majority of the total TEQs.

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