Application Note GCMS-06

Analysis of Persistent Organic Pollutants (POPs) in Silver Gull Eggs Using the EVOQ GC-TQ System

Abstract

The use of whole seabird egg for environmental contaminant testing is well established. In this study, the levels of organochlorine pesticides (OCPs), a significant group of persistent organic pesticides (POPs), were investigated in the eggs of silver gulls (Chroicocephalus novaehollandiea). Eggs were collected from Penguin Island, a small coastal island approximately 42 km south of Perth, Western Australia and 600m off the mainland coast. Egg samples were initially separated into individual yolk, albumen and eggshell components, subsequently measured and freeze-dried. The components were extracted using a modified QuEChERS method. Matrix matched standards were prepared using extracted yolk, albumen and eggshell from commercially available chicken eggs.

Authors

- Robyn Pryor, Murdoch University, Murdoch Australia

Keywords	Instrumentation and Software
Persistent Organic Pollutants (POPs)	EVOQ GC-TQ
organochlorine pesticides (OCPs)	
GC-MS/MS	

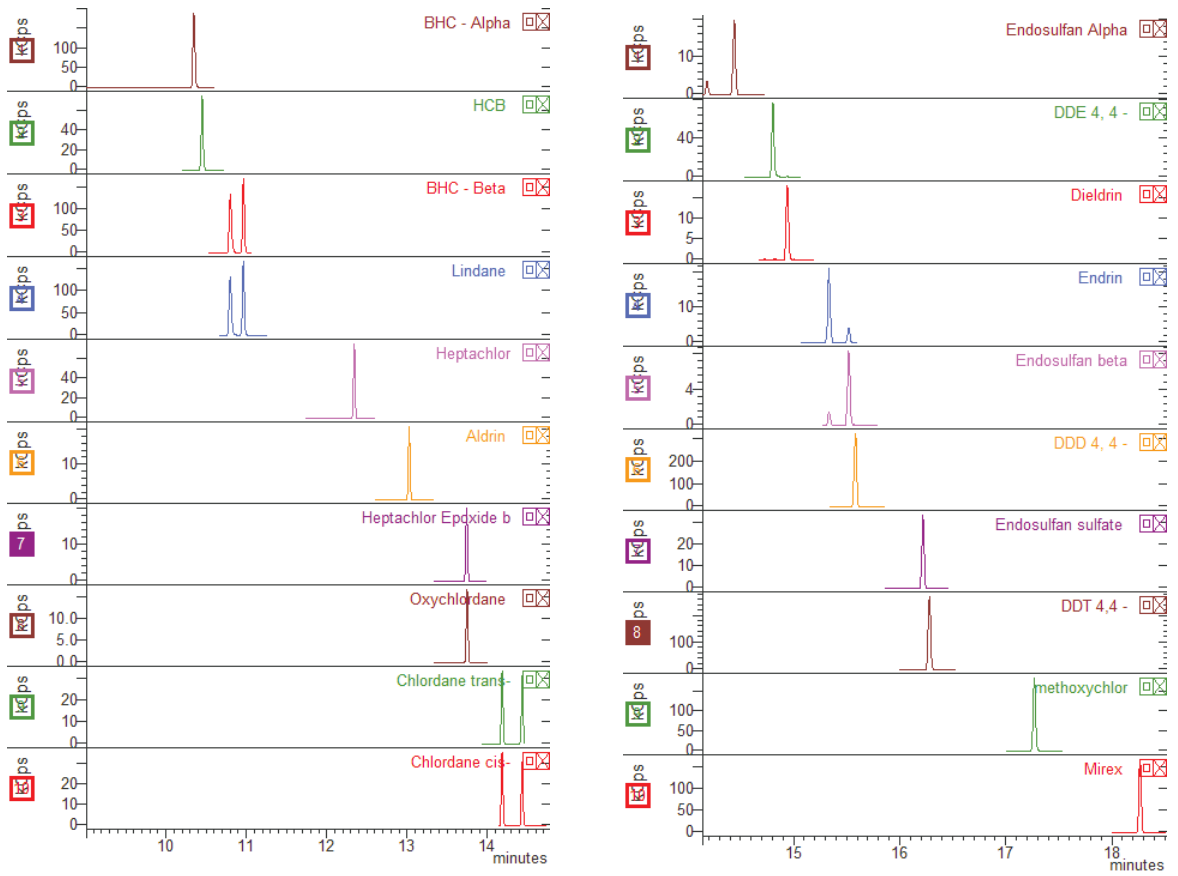


Figure 1: Example chromatogram of the 20 OCP at 20 ng/mL

Introduction

The levels of 20 common OCP contaminants including DDT and its degradation components DDE and DDD were measured in the silver gull egg yolk, albumen, and shell. The compound DDE was detected in all 35 egg yolks and most of the egg albumens. Contaminants levels were the highest in the yolks compared to the other egg parts. Dieldrin and DDT were also detected in some of the egg yolks (and DDT in a small number of albumin samples) which suggested different feeding patterns for some of the females. In addition, DDE residues were also detected in the egg shell of two of the eggs. This study shows that it is possible to use egg shells as indicators of environmental levels of persistent organic pollutants such as OCPs. This is particularly beneficial for the sampling of endangered species as it provides a completely non-invasive method for contaminant testing using discarded eggshells.

Experimental

Sample Preparation

QuEChERS extraction was used to as a sample prep for the chicken and gull yolk, albumin and egg shells. Acenaphtene-D10, Phenanthrene-D10, and Chrysene-D12 were added to the samples and standards matrix for recovery calculations. Triphenylphosphate was used as an internal standard.

The OCP calibration standards were prepared using egg, yolk, albumin, and egg shell matrix to create matrix matched standards with the following concentrations: 0.5, 1, 2, 5, 10, 20, and 50 ng/mL. For each of the different matrices calibration curves were created.

Gas Chromatography

Column: Restek Rxi-5sil MS 30m X 0.25mm X 0.25 µm with integra-Guard (10 m x 0.25mm)

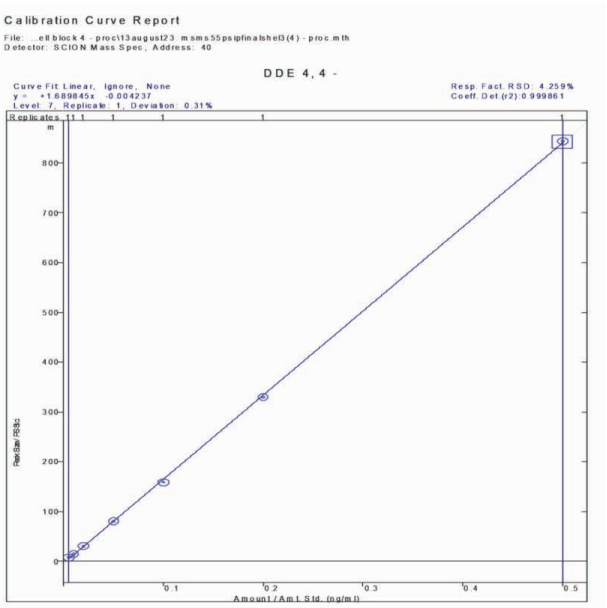
Compound			MRM 1			MRM 2			MRM 3		
In Order of Elution	**RT**	**RT Window**	**Prec**	**Prod**	**CID (V)**	**Prec**	**Prod**	**CID (V)**	**Prec**	**Prod**	**CID (V)**
Acenaphthene-D10	8.37	1.0	164	160	30	164	162	30	164	134	30
BHC-Alpha	10.33	0.5	181	145	15	219	183	10	183	147	15
HCB	10.44	0.5	284	214	35	284	249	15	286	214	30
BHC-Beta	10.79	0.5	181	145	15	219	183	10	183	147	15
Lindane	10.95	0.5	181	145	15	219	183	10	183	147	15
Phenanthrene-D10	11.22	1.0	188	188	10	188	160	25			
Heptachlor	13.02	0.5	274	239	15	272	237	20	274	237	5
Aldrin	13.73	0.5	263	193	25	263	191	30	263	226	20
Heptachlor Epoxide b	13.74	0.5	355	264	15	351	261	15	353	263	15
Oxychlordane	14.18	0.5	187	123	10	387	287	15			
Chlordane-trans	14.42	0.5	373	266	20	373	301	10	375	266	20
Chlordane-cis	14.43	0.5	373	266	20	373	301	10	375	266	20
Endosulfan Alpha	14.79	0.5	241	206	10	239	204	15			
DDE 4,4	14.93	0.5	246	176	20	246	211	20			
Dieldrin	15.33	0.5	277	241	10	263	193	30	277	206	20
Endrin	15.51	0.5	263	191	30	263	193	35	281	245	10
Endosulfan beta	15.57	0.5	239	204	15	241	170	25	241	205	20
DDD 4,4	16.21	0.5	235	165	15	235	199	15	237	165	25
Endosulfan Sulfate	16.27	0.5	272	237	15	274	238	15	387	253	10
DDT 4,4	16.27	0.5	235	165	15	235	200	10	237	165	25
Triphenylphosphate	16.56	0.5	326	326	10	326	169	10			
Methoxychlor	17.25	0.5	227	141	30	227	169	20	227	212	10
Chrysene-D12	17.25	1.0	240	240	10	240	236	35			
Mirex	18.25	0.5	272	237	20	274	237	15	274	239	15

Table 1: The retention time and MRM transitions for the organochlorine compounds, the recovery internal standards and instrument internal standard.

Compound	R^2 – value Yolks	R^2 – value Albumin	R^2 – value egg shell
BHC-alpha	0.999752	0.999903	0.999726
HCB	0.998297	0.999842	0.99878
BHC-beta	0.999904	0.999743	0.999326
Lindane	0.999995	0.999911	0.999779
Heptachlor	0.999436	0.999848	0.999813
Aldrin	0.999637	0.999736	0.998318
Heptachlor epoxide b	0.999248	0.99985	0.999239
Oxychlordane	0.999883	0.999766	0.999574
Chlordane-trans	0.999845	0.999954	0.99972
Chlordane-cis	0.999762	0.999682	0.999203
Endosulfan alpha	0.999468	0.999719	0.99887
DDE 4, 4-	0.997485	0.999952	0.999861
Dieldrin	0.99977	0.999839	0.999407
Endrin	0.99962	0.999953	0.999668
Endosulphan beta	0.999756	0.999971	0.99933
DDD 4, 4-	0.999228	0.999962	0.999204
Endosulphan sulphate	0.999676	0.999787	0.999377
DDT 4, 4-	0.998737	0.999886	0.999118
Methoxychlor	0.998952	0.999449	0.997674
Mirex	0.999636	0.999565	0.999458

Table 2: r^2 values for the separate calibration curves

a



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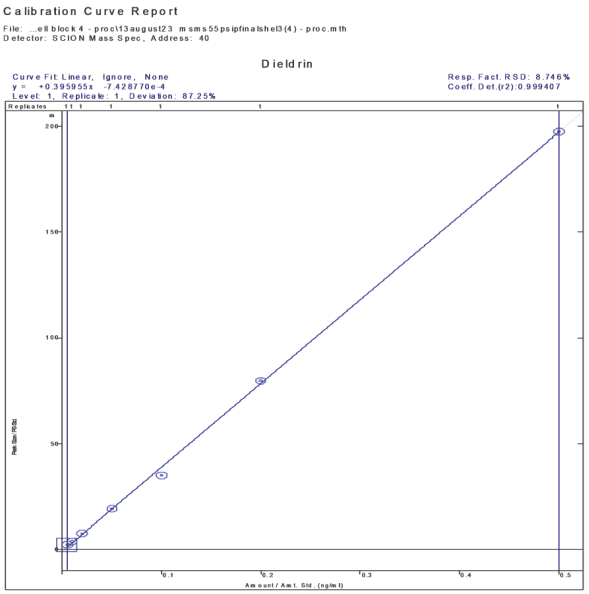

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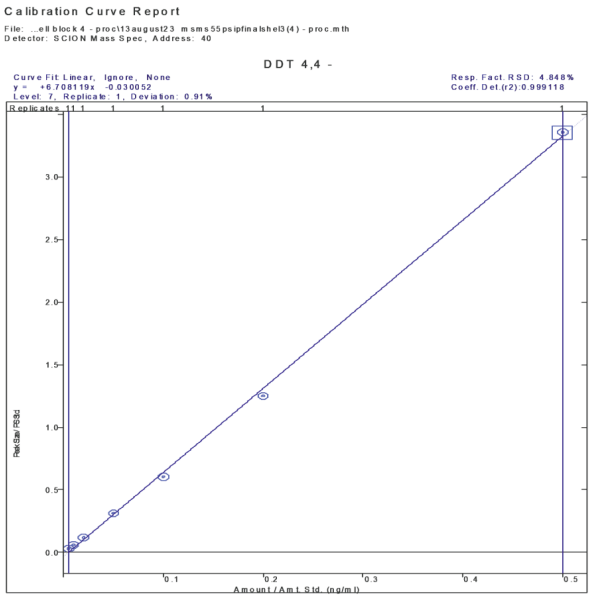

Figure 2: Calibration curves for DDE, Dieldrin and DDT in Matrix matched egg shells standards

Injection:4µL splitless injection with a 55psi pressure pulse
He Flow rate: 1.1 mL/min
Injector temp: 250°C
Column temperature Gradient:
80 °C (3 min.) 30 °C/min. to 150°C 10 °C/min. to 300°C (10 min.)

Mass Spectrometry (EVOQ GC-TQ)

Transfer line temperature: 270 °C
Ion source temperature: 200°C
Manifold temperature 40°C
CID gas: Argon at 1.5mTorr

OCP levels in Silver Gull eggs on Penguin Island

Three OCP compounds – DDE, dieldrin and DDT – were detected in the eggs of silver gulls on Penguin Island. Each of these three compounds was detected in some or all of the yolk samples. DDE was detected in each of the egg yolks. Concentrations ranged from 0.47ng/mL (2.5ppb wet weight) to 1.38ng/mL (7.5ppb wet weight). The levels of DDT in the egg yolks ranged from 0.003ng/mL (0.016ppb wet weight) to 0.83ng/mL (4.5ppb wet weight). Dieldrin was found to have the highest concentrations of any of the analytes in the silver gull eggs. Levels of dieldrin in the yolks ranged from 0.84ng/mL (4.5ppb wet weight) to 2.85ng/mL (15.4ppb wet weight).

Only the compounds DDE and DDT were found in the albumen samples. The compound DDE was detected at trace levels in nearly all the albumen samples, and concentrations ranged from 0.004ng/mL (0.02ppb wet weight) to 0.11ng/mL (0.46ppb wet weight). Levels of DDT were much higher than DDE, but were only detected in four samples. The DDT concentrations in albumen samples ranged from 0.04ng/mL (0.17ppb wet weight) to 0.29ng/mL (1.22ppb wet weight).

The compound DDE was detected in two of the eggshell samples at levels of 0.13ng/mL (1.9ppb wet weight) and 0.14ng/mL (2.1ppb wet weight). Concentrations of DDE ad DDT were generally highest in the yolk samples and lowest in the albumen samples, possibly due to the higher lipid content of the yolks (Burley & Vadehra, 1989).

Conclusion

Although most organochlorine pesticides were banned from use in developed countries during the 1970s and 1980s, these compounds are still found in a wide variety of biotic tissues and environmental samples throughout the world (Cipro et al., 2013; Lewis et al., 2007; Mallory & Braune, 2012). Seabirds, in particular, are prone to bioaccumulation of persistent OCPs due to their relatively large size, longevity, and position at a high trophic level.
Reliable and accurate methods for the analysis of OCPs are important for the continued monitoring of temporal and spatial changes associated with these biologically important compounds.

This study shows very low levels (0.06 ppb DDT in dry weight) of OCPs can be measured in complex matrices such as yolk, albumin and egg shells.

Another significant outcome of this study is the detection of DDE in the eggshells of silver gulls. This detection in eggshells has demonstrated the potential for the establishment of a new, non-destructive method of contaminant testing by using discarded eggshells from hatched eggs. Endangered species can benefit from such non-invasive methodology. Future investigations to further optimise the extraction methods in eggshells are very much needed.

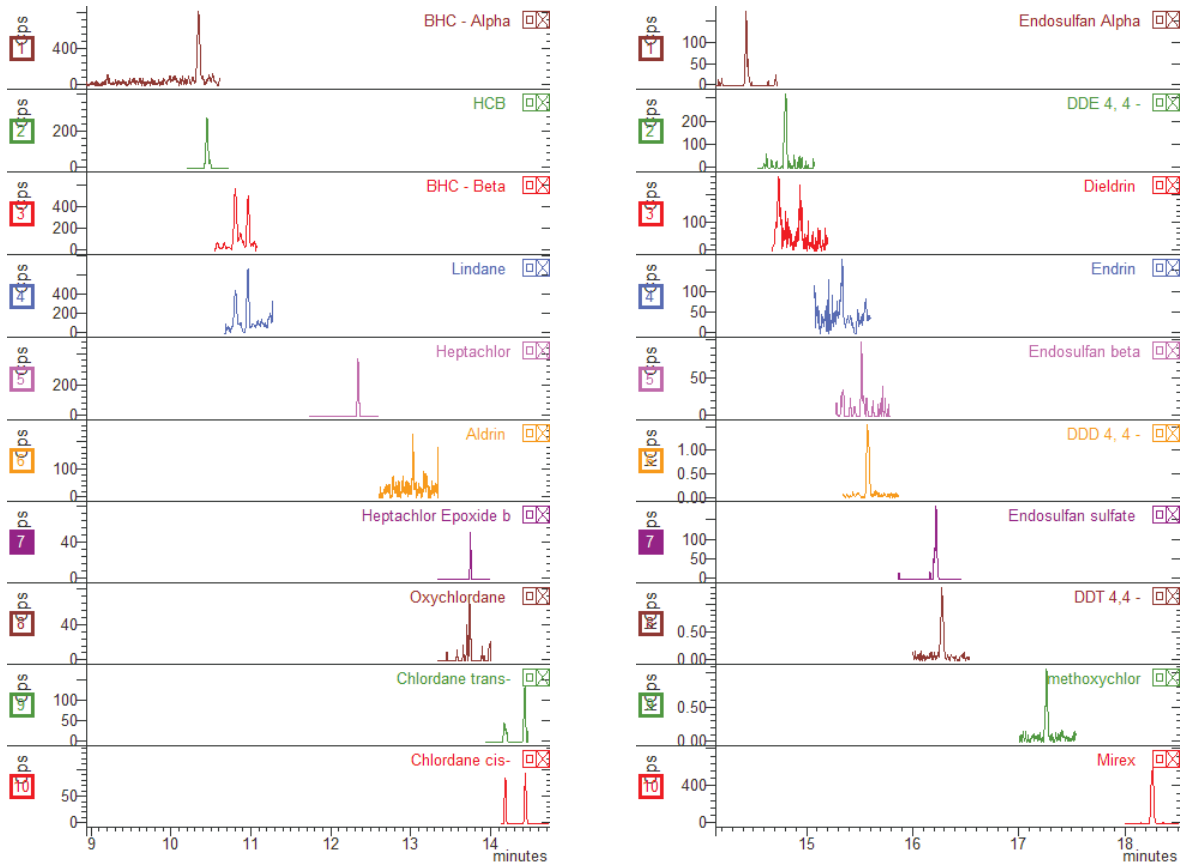

Figure 3: Example chromatogram of 0.5 ng/mL OCP Calibration standard in egg shell matched matrix

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Bruker Daltonik GmbH

Bremen · Germany
Phone +49 (0)421-2205-0
Fax +49 (0)421-2205-103

Bruker Daltonics Inc.

Billerica, MA · USA
Phone +1 (978) 663-3660
Fax +1 (978) 667-5993

ms.sales.bdal@bruker.com - www.bruker.com