PERFLUOROOCTANE SULFONATES AND OTHER FLUOROCHEMICALS IN WATERBIRD EGGS IN HONG KONG

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Abstract

Waterbirds are one of the most conspicuous groups of animals in the coastal environment in Hong Kong, and have a high conservation value in the Hong Kong marine ecosystem. In recent years, there has been increasing evidence that the Mai Po and Inner Deep Bay areas are under threat from a wide range of environmental contaminants. Perfluorinated compounds (PFCs) are a group of chemicals that are causing increasing concern. Egg samples from night herons and great egrets were collected from A Chau，Hong Kong in 2006 for the investigation on PFC residues in waterbird eggs. The night heron eggs had a higher PFOS concentration than the great egret eggs (146 and 39.2 ng/g wet wt, respectively), which is comparable to reported concentrations in other avian species in other countries (104 ng/g wet wt. and 67 ng/g wet wt.). The total PFC concentrations were higher in the night heron eggs, with PFOS being the dominant PFC, followed by PFUnDA, PFDoDA, PFDA, and PFNA. PFOS was also found to be the dominant PFC in the great egret eggs, followed by PFUnDA, PFDoDA, PFDA, PFNA and PFOSA.

Introduction

Waterbirds are one of the most conspicuous groups of animals in the coastal environment in Hong Kong, and have a high conservation value in the Hong Kong marine ecosystem. In recent years, there has been increasing evidence that the Mai Po and Inner Deep Bay areas are under threat from a wide range of environmental contaminants. Specifically, the northwestern part of Hong Kong receives a rich supply of sediments with a high organic and inorganic content from the Pearl River and nearby local streams High levels of pesticides, including compounds that have been banned in Hong Kong (e.g., DDT), have been detected in marine sediments around the Deep Bay area. The occurrence of these chemicals may be attributable to sources of contamination in the Chinese mainland.[1,2] Sediments with a high metal content have also been found in the Pearl River Delta (PRD) region.[3] Toxic metals, in combination with a wide range of persistent organic pollutants, have probably resulted in a deterioration of environmental quality in the western waters of Hong Kong, including the ecologically important Mai Po and Inner Deep Bay RAMSAR site.

Perfluorinated compounds (PFCs) are a group of chemicals that are causing increasing concern. The wide application of this group of chemicals has drawn the attention of scientists and governments, because there is much evidence that they have become ubiquitous in the air, seawater, drinking water, various biota, and even human tissues.[4,5,6,7,8,9] Recent studies have demonstrated that PFCs are present in the coastal seawater around Hong Kong and the Pearl River Delta,[4,5] and that they are bioaccummulative in biota.[10] To date, there is no information about the degree of PFC contamination in the biota in Hong Kong. Waterbird eggs are frequently used as biomonitoring tools to measure contaminant levels in Hong Kong because they represent the levels of contaminants in female birds.[11,12] Here, we report some initial findings on PFC residues in waterbird eggs that were collected in Hong Kong.

Materials and Methods

Egg samples from night herons and great egrets were collected from A Chau in 2006 with permission from the Agricultural, Fisheries and Conservation Department of Hong Kong (Figure 1). The collected eggs were wrapped in aluminum foil, transferred to clean glass jars, and stored at -20^{o}C in the laboratory at the City University. Individual PFCs were extracted using an ion-pairing method and were reduced to 1 mL. In addition, 0.5 mL of the sample extract was subjected to solid phase extraction (SPE) cleanup. The concentrations of perfluorinated sulfonates (PFOS, perfluorohexane sulfonate – PFHxS), perfluorooctanesulfonamide (PFOSA), and perfluorinated carboxylates (Perfluorohexanoic acid – PFHxA, perfluoroheptanoic acid – PFHpA, PFOA, perfluorononanoic acid – PFNA, perfluorodecanoic acid – PFDA, perfluoroundecanoic acid – PFUnDA, and perfluorododecanoic acid – PFDoDA, perfluorotetradecanoic acid), and some other PFCs were determined by using HPLC-MS/MS. The separation of the analytes was performed by using an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) that was interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) and operated in the electro-spray negative mode. A 10-μL aliquot of extract was injected onto a Keystone Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 μm, 100Å pore size, endcapped) with 2 mM of ammonium acetate and methanol as the mobile phases. The details of the procedure for LC-MS/MS are reported elsewhere.[13]

Results and Discussion

Blank and recovery tests were conducted on each batch of sample, and the PFOS, PFHxS, PFOSA, PFDoDA, PFUnDA, PFDA, PFNA, and PFOA concentrations were measured. The PFBS, PFOcDA, PFHpA, PFHxA, FTUCA, and FTCA concentrations were all below LOQ. The blank and recovery test results and PFC concentrations are summarized in Table 1.

The total PFC concentrations were higher in the night heron eggs, with PFOS being the dominant PFC, followed by PFUnDA, PFDoDA, PFDA, and PFNA. PFOS was also found to be the dominant PFC in the great egret eggs, followed by PFUnDA, PFDoDA, PFDA, PFNA and PFOSA. The differences in

PFOS concentration may be attributable to species-specific bioaccumulation or different feeding habits, because great egrets feed on fish, amphibians, crustaceans, aquatic and terrestrial insects, snakes, and small mammals such as mice, whereas night herons feed mainly on fish. However, the PFC composition profiles of the two species were similar despite their different feeding habits, with around 80% of the PFCs consisting of PFOS, around 10% being PFUnDA, and the rest comprising PFDoDA, PFDA, and PFNA. The similar PFC composition profiles suggest that the exposure pathways to the two species may be similar.

The night heron eggs had a higher PFOS concentration than the great egret eggs (146 and 39.2 ng/g wet wt, respectively), which is comparable to reported concentrations in other avian species in other countries (104 ng/g wet wt.[14] and 67 ng/g wet wt[8].). A number of studies have reported the PFOS concentration in egg samples, but few studies have reported the levels of other PFCs. For example, Tao et al. reported the occurrence of PFOS, PFDoDA, PFUnDA, and PFDA at similar concentrations in albatross eggs.[15] Albatross eggs showed different composition profiles from waterbird eggs in Hong Kong (PFOS was the dominant PFC in Hong Kong), suggesting different sources of contamination or species-specific bioaccumulation. Further investigations are needed to clarify these points.

To our knowledge, this is the first report on PFC concentrations in waterbird eggs in the Pearl River Delta. Further investigations should be conducted to identify the sources of contamination, and to make a preliminary risk assessment to evaluate the health risk to waterbirds of exposure to PFCs in south China.

Reference

1. Richardson BJ, Zheng GJ *Chemoshpere* 1999; 39: 61-71.
2. Richardson BJ, Lam PKS, Wu RSS In: C Sheppard (Ed), *Seas at the Millennium: an Environmental* Evaluation. 2000 Vol. II. Elsevier Science, pp 535-547.
3. Cheung KC, Poon BHT, Lan CY, Wong MH *Chemosphere* 2003; 52: 1431-1440.
4. Martin JW, Muir DCG, Moody CA, Ellis DA, Kwan WC, Solomon KR, Mabury SA *Anal. Chem.* 2002; 74: 584-590.
5. So MK, Taniyasu S, Yamashita N, Giesy JP, Zheng J, Fang Z, Im SH, Lam PKS *Environ. Sci. Technol.* 2004; 38: 4056-4063.
6. So MK, Miyake Y, Yeung WY, Ho YM, Taniyasu S, Rostkowski, P, Yamashita N, Zhou BS, Shi XJ, Wang JX, Giesy JP, Yu H, Lam PKS *Chemosphere* (In press).
7. Yamashita N, Kannan K, Taniyasu S, Horii Y, Okazawa T, Petrick G, Gamo T *Environ. Sci. Technol.* 2004; 38: 5522-5528.
8. Kannan K, Corsolini S, Falandysz J, Oehme G, Focardi S, Giesy JP *Environ. Sci. Technol.* 2002; 36: 3210-3216.
9. Yeung LW, So MK, Jiang G, Taniyasu S, Yamashita N, Song M, Wu Y, Li J, Giesy JP, Guruge KS, Lam PK *Environ. Sci. Technol.* 2006; 40: 715-720.
10. Sinclair E, Mayack DT, Kenneth R, Yamashita N, Kannan K *Arch. Environ. Con. Toxicol.* 2006; 50: 398-410.
11. Lam JCW, Tanabe S, Lam MHW, Lam PKS *Environ. Poll.* 2006; 135: 481-490.
12. Lam PKS, Connell DW, Lam MHW 2001. *Study on the effect of water pollution on the breeding success of Ardeids.* Final report. Submitted to the Agriculture, Fisheries and Conservation Department, Hong Kong SAR Government.
13. Taniyasu S, Kannan K, So MK, Gulkowska A, Sinclair E, Okazawa, T, Yamashita N *J Chromatogr A* 2005; 1093: 89-97.

14. Verreaault J, Houde M, Gabrielsen GW, Berger U, Haukås M, Letcher RJ, Muir DCG *Environ. Sci. Technol.* 2005; 39: 7439-7445.
15. Tao L, Kannan K, Kajiwara N, Costa MM, Fillmann G, Takahashi S, Tanabe S *Environ. Sci. Technol*. 2006; 40: 7642-7648.

Figure 1. Sampling location of water bird eggs in Hong Kong.

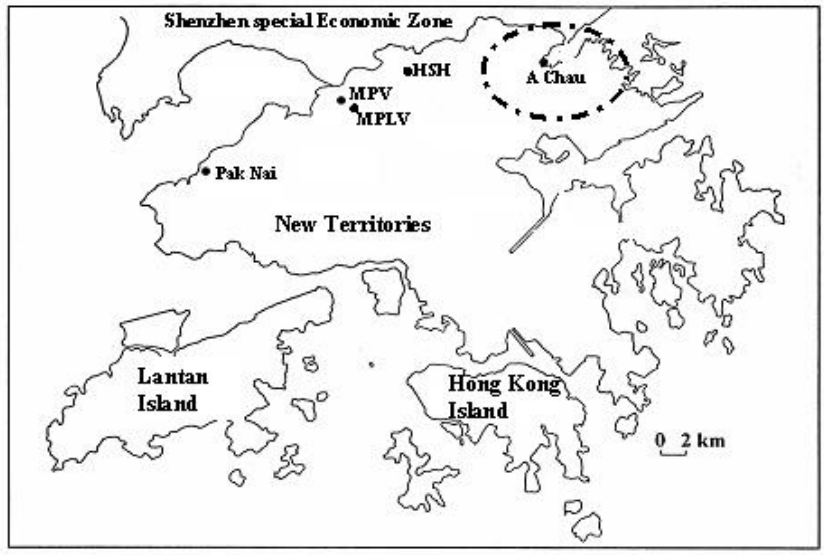

Table 1. Blank, recoveries and concentrations of PFCs in Night Heron and Great Egret egg samples (ng/g wet wt.).

		PFOS	PFHxS	PFOSA	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	Total PFC
	Blank	**<0.08**	**<0.08**	**<0.4**	**<0.016**	**<0.016**	**<0.4**	**<0.08**	**<0.08**	
n=3	**Mean Rec.**	103	96	66	83	98	95	100	87	
	S.D.	10	6	14	17	4	5	2	15	
n=2	**Matrix spike rec. mean**	98[a]	100	104	108	113	94	100	109	
	S.D.	7	4	1	1	1	2	1	1	
Night Heron	**Mean**	146			18.8	21.2	10.4	0.951		198
n=5	**S.D.**	112			23.4	12.4	6.62	0.396		147
	Min	42.6	<0.08	<0.4	2.69	6.69	2.73	0.241	<0.08	55
	Max	328	0.418	2.48	69.8	42.8	21.5	1.33	0.123	466
Great Egret	**Mean**	39.2			2.68	4.89	1.28	0.512		48.8
n=5	**S.D.**	11.1			0.751	1.79	0.339	0.166		14.1
	Min	27.6	<0.08	<0.4	1.63	3.19	0.875	0.341	<0.08	34.7
	Max	58.3	0.111		3.97	7.99	1.80	0.850	0.112	73.1

[a]: matrix spike recovery of PFOS was based on C_{13} PFOS