

Available online at www.sciencedirect.com



Marine Pollution Bulletin 50 (2005) 1713-1744

BUILLETIN

POILILIUMION

MARINE

www.elsevier.com/locate/marpolbul

Baseline

Edited by Bruce J. Richardson

The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline—The New Format and Content' (Mar. Pollut. Bull. 42, 703–704).

Petroleum hydrocarbons, polycyclic aromatic hydrocarbons, organochlorine pesticides and polychlorinated biphenyls in tissues of Indo-Pacific humpback dolphins from south China waters

Clement C.M. Leung ^a, Thomas A. Jefferson ^b, Samuel K. Hung ^c, Gene J. Zheng ^a, Leo W.Y. Yeung ^a, Bruce J. Richardson ^a, Paul K.S. Lam ^{a,*}

^a Department of Biology and Chemistry, Centre for Coastal Pollution and Conservation, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

^b Southwest Fisheries Center, NOAA Fisheries, 8604 La Jolla Shores Drive, La Jolla, CA 92037, USA

^c Hong Kong Cetacean Research Project, 12 Kak Tin Kung Miu Village, Tai Wai, New Territories, Hong Kong, China

Indo-Pacific humpback dolphins (*Sousa chinensis*) are long-term residents of Hong Kong waters (Parsons et al., 1995). They are of special conservation value, and are protected under the Convention on International Trade in Endangered Species of Wild Fauna and Flora. The size of the breeding dolphin population in the Pearl River Delta, south China, is estimated to be around 1400 individuals, and a total of 265 animals has been identified in Hong Kong waters since 1995 (Hung et al., 2004). As these animals occupy the highest trophic level in the local marine food chain, and have a relatively long life span, they tend to accumulate significant amounts of various pollutants (Kemper et al., 1994).

The Hong Kong and Pearl River Delta area is undergoing a massive transformation, and has become the fastest growing manufacturing and industrial hub of the world. Due to the widespread occurrence of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and petroleum hydrocarbons (PHCs) in the region, it is instructive to assess the risks of these contaminants to the local Indo-Pacific humpback dolphins. In this study, blubber samples were collected from five free ranging living Indo-Pacific humpback dolphins from Hong Kong, four stranded dolphins from Xiamen, Fujian Province, and one stranded specimen from Zhuhai, Guangdong Province (Fig. 1 and Table 1). To our knowledge, this is the first study on concentrations of persistent organic pollutants in dolphin samples from Xiamen and Zhuhai. This study aims to provide preliminary data on the concentrations of common persistent organic pollutants in the Indo-Pacific humpback dolphins in south China waters for future risk assessments.

Biopsy samples (skin and blubber; about $0.2 \text{ cm} \times 0.2 \text{ cm} \times 0.2 \text{ cm}$) were collected from living Indo-Pacific humpback dolphins (*S. chinensis*) in the estuarine northwestern waters of Hong Kong. The samples were taken using biopsy darts launched with a Barnett Ranger RX-150 crossbow, with 68-kg draw weight. This crossbow shoots arrows at a speed of 69 m s⁻¹. A red dot scope was used to help in aiming. The ACC carbon fiber biopsy darts used were produced by Ceta-Dart, and tips were made at the Scripps Institute of Oceanography (SIO) machine shop. The biopsy tips were immersed in 10%

^{*} Corresponding author. Tel.: +852 2788 7681; fax: +852 2788 7406. *E-mail address:* bhpksl@cityu.edu.hk (P.K.S. Lam).



Fig. 1. Map showing study locations.

Table 1 Information on Indo-Pacific humpback dolphin samples collected from Xiamen and Zhuhai

Sample no.	Site	Date of collection	Sex	Weight (kg)	Length (cm)	Age
X1 X2 X3 X4	Xiamen Xiamen Xiamen	29/4/2004 6/1/2003 15/8/2002 2/7/2003	Female Female Female Female	84 213 250 NA	200 238 249 105	NA NA 11 NA

NA: Not available.

alcohol prior to being used for sampling to prevent the chances of cross-contamination of samples and of infection. Biopsy specimens were taken in the thoracic area anterior to the dorsal fin. All tissues collected were kept on ice, and transferred to the laboratory. The skin sample was separated from the blubber using a single edge razor blade, and the skin was used for sex determination by Kelly Robertson and Carrie Le Duc at the Southwest Fisheries Centre, La Jolla, California. The blubber samples were stored at -20 °C until subsequent chemical analyses. In addition, blubber samples were removed using a pre-cleaned stainless steel knife from specimens of Indo-Pacific humpback dolphins stranded in Xiamen (a city in Fujian province, southeastern China) and Zhuhai (a city on the western side of the Pearl River Delta). These blubber samples were analyzed together with the biopsy samples from live dolphins.

The analytical methods followed those described in Richardson and Zheng (1999), Zheng et al. (2004) and Fung et al. (2004). Briefly, about 0.2 g of subcutaneous blubber sample was spiked with 1 ml each of internal standards, decachlorobiphenyl (1012 ng ml⁻¹), C₂₂ (8160 ng ml⁻¹) and *m*-terphenyl (10,490 ng ml⁻¹). The sample was homogenized with 30 ml dichloromethane (DCM) using a K-Ultra-Turrax T-25 homogenizer at a speed of 1100 rpm until all the blubber tissue was dissolved. After filtration using a 70 mm pore size glass fiber filter (Advantec), the volume of each sample was reduced in a rotary

evaporator, and then passed through a silica gel column to remove impurities and lipids. After eluting PHCs from the column with 15 ml of hexane, the column was further eluted with a mixture of hexane:dichloromethane (8:2) and DCM for PCBs and OCPs, and PAHs.

Organochlorines in the second fraction were quantified by GC- μ ECD (Hewlett Packard 6890 II series) equipped with an Agilent 7683 series automatic sampler. The GC column employed was a DB-5 capillary column (J&W Scientific Inc., USA, 30 m × 0.25 mm internal diameter × 0.25 µm film thickness). The column oven temperature was programmed as follows: 110 °C hold for 2 min, increased to 180 °C at a rate of 10 °C min⁻¹, and then increased to 280 °C at a rate of 5 °C min⁻¹ and held for 14 min. Injector and detector temperatures were set at 250 °C. Nitrogen was used as the carrier gas.

PCBs, HCHs, HCB, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, kepone, chlordanes, and DDT and its metabolites were measured. Peaks of individual compounds were identified from those of their corresponding external standards. Organochlorine concentrations were calculated from the peak areas of individual compounds relative to the peak area of the internal standard. The PCB standard (SRM 2262) contained 28 congeners (PCB 1, 8, 18, 28, 29, 44, 50, 52, 66, 77, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 194, 195, 200, 206). Concentrations of individually resolved PCB congeners were summed, and then multiplied by 2 to obtain total PCB concentration. A procedural blank was analyzed with every set of 6 samples to check for interfering compounds and correction was made, if necessary. Total DDTs represented the sum of p,p'-DDT, o,p-DDT, *p*,*p*'-DDD, *o*,*p*-DDD, *p*,*p*'-DDE and *o*,*p*-DDE. Chlordanes (CHLs) included cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, and oxychlordane while total HCHs included α , β , γ and δ isomers. Recoveries of target analytes using this analytical method were $99 \pm 2.0\%$ for PCBs, $95 \pm 7.5\%$ for DDTs, $96 \pm 7.7\%$ for HCHs, $100 \pm 4.7\%$ for CHLs, $94 \pm 5.9\%$ for HCB.

A Hewlett Packard 6890 series gas chromatograph with a 30 m Ultra-2 fused silica capillary column (0.2 mm diameter and 0.33 μ m thickness film; 95% dimethyl–5% polysiloxane) was used for the analysis of petroleum hydrocarbons. Total amounts of *n*-alkanes and UCM were counted as total petroleum hydrocarbons. For the 15 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1, 2,3-*cd*)pyrene, dibenzo(1,2,5,6)-perylene and benzo(*g*,*h*, *i*) perylene), gas chromatography–mass spectrometry (GC–MS) with selected ion monitoring (SIM) was used with *m*-terphenyl as the internal standard (Pruell and Quinn, 1985; Zheng and Quinn, 1988).

All specimens were run in batches which included method blanks, spiked samples and standard reference materials SRM 2974 and HS-6 (National Institute of Standards and Technology, Gaithersburg, MD, USA). Recoveries of total

1715

Table 2

Mean concentrations of OC pesticides and PCBs in Dolphin blubber from Hong Kong, Xiamen and Zhuhai waters (ng g^{-1} wet weight)

Location	Hong Kong $(n = 5)$	Xiamen $(n = 4)$	Zhuhai $(n = 1)$	
α-HCH	24.7	26.5	2	
β-ΗCΗ	910.4	129.3	nd ^a	
γ-HCH	197	38.1	17.1	
δ-НСН	32.6	33.6	13.7	
Total HCHs	1164.7	227.6	32.8	
HCB	42.7	62.7	90.1	
Heptachlor	93.7	142.6	32.3	
HE	248.4	27.6	28.1	
Aldrin	39.7	12	nd ^a	
Dieldrin	2703.1	5149.3	nd ^a	
Endrin	624.9	991.4	758.7	
Kepone	656.4	nd^{a}	nd ^a	
γ-Chlordane	108	236.6	221.7	
α-Chlordane	150.5	12.9	nd ^a	
Total Chlordanes	258.6	249.5	221.7	
o,p-DDE	31.3	nd ^a	nd ^a	
p,p'-DDE	3927.7	7582.8	8455.9	
o,p'-DDD	178.2	13.2	7.2	
p,p'-DDD	1858.8	87.1	11.5	
o,p'-DDT	860.4	10356.9	8619.2	
p,p'-DDT	2254.2	41501.9	27273.3	
Total DDTs	9110.5	59541.9	44367.1	
Total PCBs	19978.6	251.4	69.4	

^a Not detected (detection limit = 0.05 ng g^{-1}).

PAHs in spiked samples ranged from 82.5% to 88.4%, while recoveries for SRM 2974 and HS-6 ranged from 88.2% to 96.4%. For petroleum hydrocarbons, recoveries of fuel oil and kerosene were around 69% and 57%, respectively. Concentrations were not corrected for recovery rates. All results were expressed on a wet weight (w.w.) basis.

Concentrations of OCPs and PCBs in dolphin blubber samples are summarized in Table 2. For the Hong Kong samples, the average organochlorine concentrations in male animals were, in general, several times higher than those of the females, especially for total HCHs, total DDTs and Dieldrin. Concentrations of total HCHs in male dolphins ranged from 182.5 to 3085.3 ng g^{-1} (mean: 1574.1 ng g⁻¹; n = 3), while those in female dolphins were 343.8 and 757.4 ng g^{-1} . For total chlordanes, male dolphins had concentrations ranging from of 276.1 to 488.7 ng g^{-1} . and concentrations of the two female specimens were 108.0 and 105.8 ng g^{-1} . Concentrations of total PCBs were relatively high, ranging from 11,176.4 to 40,824.3 ng g^{-1} in the males to 5296.4 and 14,260.0 ng g^{-1} in the female specimens. Concentrations of total PAHs in the male dolphins (ranging from 2413.1 to 4663.2 ng g^{-1}) were higher than those in female dolphins (2263.1 and 2986.2 ng g^{-1}). There was no significant difference in concentrations of petroleum hydrocarbons between male $(18.2-32.3 \text{ mg g}^{-1})$ and female $(25.3 \text{ and } 28.4 \text{ mg g}^{-1})$ dolphins.

Most of organochlorine concentrations in the Hong Kong biopsy samples were higher than those from the stranded samples in Xiamen and Zhuhai. For example, mean concentration of total HCHs in the Hong Kong biopsy samples was 1164.7 ng g⁻¹, which was about 5 times higher than those of samples from Xiamen (227.6 ng g⁻¹) and 36 times greater than that of Zhuhai (32.8 ng g⁻¹). Similarly, the mean concentration of total PCBs in the Hong Kong biopsy samples (19,978.6 ng g⁻¹) was also significantly higher than those of stranded specimens from Xiamen (251.4 ng g⁻¹) and Zhuhai (69.4 ng g⁻¹). For total chlordanes, the Hong Kong samples (258.6 ng g⁻¹) had concentrations comparable to those of the Xiamen (249.5 ng g⁻¹) and Zhuhai (221.7 ng g⁻¹) samples.

The average ratio of $DDT / \sum DDT : DDD / \sum DDT :$ $DDE/\sum DDT$ in the biopsy samples was 44:22:34. The proportion of DDE was much lower when compared to that found in marine mammals from other parts of the Pacific, where DDE typically accounts for between 70% and 95% of the total DDTs (Prudente et al., 1997). Significantly, the average ratios for the Xiamen and Zhuhai samples were 87:0:13 and 81:0:19, respectively, and the proportions of DDT in these samples were about 2-fold greater than that found in biopsy samples from Hong Kong. Furthermore, the proportion of DDE was more than 3-fold lower than the lowest value recorded in marine mammals from other parts of the Pacific (Prudente et al., 1997). The greater proportion of DDT in the blubber samples of dolphins inhabiting south China waters lends support to the suggestion that there is still continuous fresh input of DDT. The above findings are consistent with recent speculations that DDT is present as an impurity in an acaricide (mitecide) known as Dicofol, which is currently being used widely in China. Indeed, our analysis has revealed that Dicofol may contain from 1.8% to 2.4% of DDT in the formulation sold in south China (unpublished results).

Concentrations of PAHs in dolphin blubber are summarized in Table 3. All fifteen PAHs were detected in all the Hong Kong biopsy samples, as well as samples from stranded dolphins from Xiamen and Zhuhai. In the Hong Kong and Zhuhai samples, the most dominant chemical among the 15 PAHs was naphthalene, which accounted for about 33.6% and 27.5% of the total PAHs (Fig. 2). For the Xiamen sample, dibenzo(1,2,5,6) perylene was predominant, accounting for nearly 21% of the total. The seven most abundant PAHs accounted for over 83% of the total PAHs in the Hong Kong and Zhuhai samples, and nearly 93% in the Xiamen sample. Carcinogenic PAHs (chrysene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene; Kennish, 1996) in the Hong Kong, Xiamen and Zhuhai samples accounted for 16.8%, 44.8% and 27.2% of total PAHs, respectively.

Concentrations of total PAHs were highest in the Xiamen sample (6751 ng g⁻¹), followed by the Hong Kong biopsy samples (3274.6 ng g⁻¹), and were lowest in the Zhuhai sample (2761.6 ng g⁻¹). Concentrations of total PHCs were highest in the Hong Kong biopsy samples (25.1 mg g⁻¹), which was over 5 and 8 times greater than that of the Xiamen (4.81 mg g⁻¹) and Zhuhai (2.9 mg g⁻¹) samples, respectively. Table 3

Mean concentrations of 15 PAHs and PHCs in alive Dolphin blubber in Hong Kong, stranded dolphin blubber in Xiamen and Zhuhai waters (ng g^{-1}	wet
weight for PAHs, mg g^{-1} wet weight for PHCs)	

	Hong Kong $(n = 5)$	Xiamen $(n = 4)$	Zhuhai $(n = 1)$	Carcinogenicity ^a (ATSDR ^b)
1. Naphthalene	1100.5	585.8	758.5	_
2. Acenaphthylene	717.1	117.7	188	_
3. Acenaphthene	21.3	63.6	141.7	_
4. Fluorene	108.3	65.7	37.1	_
5. Phenanthrene	17.8	98.7	132.2	_
6. Anthracene	284.1	32.5	29.1	_
7. Fluoranthene	24.4	628	53.3	_
8. Pyrene	312.7	266.9	82	_
9. Chrysene	150.2	374.7	147.8	*
10. Benzo(b)fluoranthene	121.6	338.6	225.9	+
11. Benzo(k)fluoranthene	26.2	249.5	197.6	_
12. Benzo(<i>a</i>)pyrene	8.8	1173.5	178.7	+
13. Indeno(1,2,3- <i>cd</i>)pyrene	269.9	1139.4	197.6	+
14. Dibenzo(1,2,5,6)perylene	43.1	1384.5	237.2	_
15. $\text{Benzo}(g,h,i)$ perylene	68.7	231.8	155	_
Total PAHs	3274.6	6751	2761.6	
Total carcinogenic PAHs	550.5	3026.2	750	
Total PHCs	25.1	4.81	2.9	

^a -= not carcinogenic; ^{*} = weakly carcinogenic; += strongly carcinogenic.

^b Available at http://www.atsdr.cdc.gov/HAC/PHA/popile/pop_p4.html.



Fig. 2. PAH fingerprints in dolphin blubber samples from Hong Kong, Xiamen and Zhuhai.

Dolphins are ranked top of marine food chains, and have a special preference for estuarine fish in the families of Engraulidae, Sciaenidae and Clupeidae (Jefferson, 2000). It is conceivable that the differences in persistent organic pollutant residues in the tissues of dolphins are attributable to the differences in diet preference and composition.

There are only limited data on PAH concentrations in dolphin or other cetacean tissues in the literature (e.g., Law and Whinnett, 1992; Lake et al., 1995; Martineau et al., 1994; Zitko et al., 1998; Holsbeek et al., 1999; Marsili et al., 1997; Hellou et al., 1990, 1991). In this study, the median value of PAH concentrations in the Hong Kong, Xiamen and Zhuhai samples were 2.99, 6.68 and 2.76 μ g g⁻¹, respectively, while the corresponding maximum values were 4.66, 8.53 and 2.76 μ g g⁻¹. Amongst the three locations, samples from Xiamen had highest

concentrations of total and carcinogenic PAHs. This observation may reflect a relatively high level of PAH contamination in the marine environment of Xiamen, particularly in the semi-enclosed harbour where a number of petroleum storage tanks, oil refineries, two large power stations, and several wharfs are located. In addition, wastewaters from nearby cities, e.g., Shangming, Zhangzhou and Xiamen, also enter Xiamen Harbour via the river Jiu Long Jiang (Ou et al., 2004). These represent potentially important petrogenic and pyrolytic sources of PAHs. Live and stranded dolphin samples had similar concentrations of total PAHs. Generally, both live and stranded dolphin samples contained high concentrations of low molecular weight PAHs such as naphthalene and acenaphthylene as compared to high molecular weight PAHs, presumably reflecting the ease of uptake of the former.

Pyrolysis of carbon-based PHCs is known to produce many derivatives, including PAHs, and thus higher concentrations of PAHs may be expected to be associated with higher concentrations of PHCs. However, in this study, concentrations of PHCs in the biopsy samples were over 5-fold higher than those of the Xiamen samples, while concentrations of PAHs in the biopsy samples were nearly 2-fold lower than those of the Xiamen samples. These observations suggest that the dolphins in Xiamen could have accumulated PAHs arising from other sources in addition to the pyrolysis of PHCs.

Such sources could include the atmospheric input of PAHs from incomplete burning of fossil fuel, possibly from the two large electric power stations located in the area. It is possible that petroleum hydrocarbon contaminants may have "escaped" from decomposing tissues of stranded dolphins, and this might explain the relatively lower concentrations of PHCs found in stranded specimens as compared to biopsy samples from live dolphins. However, further studies will be needed to verify this point.

Results of this study revealed that concentrations of total DDTs were higher in the stranded dolphins from Xiamen and Zhuhai, while concentrations of total PCBs were much lower, as compared to the Hong Kong live dolphin samples. These findings are consistent with previous studies reporting a relatively high degree of DDT contamination in mainland China, but relatively low PCB levels as a result of China's short history of industrialization (Fung et al., 2004).

Concentrations of total PCBs, ranging from 5.3 to 40.8 μ g g⁻¹ (Table 4), in the blubber of live Indo-Pacific humpback dolphins in Hong Kong are similar to those previously reported in stranded Indo-Pacific humpback dolphins in Hong Kong (range: $3.3-50 \ \mu g \ g^{-1}$; Minh et al., 1999). These results suggest that PCB data from stranded specimens are still useful for ecotoxicological assessment, although decomposition is known to influence measured concentrations of certain contaminants (Borrell and Aguilar, 1990). On average, total PCB concentrations in dolphins from the Asian coastal waters were comparable to dolphins in the coastal areas of Africa, but were much lower than those from the North Pacific, South Atlantic, western Mediterranean Sea, European coastal waters and USA (Table 4).

In contrast, these values were higher than bottlenose dolphins from coastal waters of Australia (0.06 μ g g⁻¹).

The concentration of total PCBs in the Zhuhai sample $(0.07 \ \mu g \ g^{-1})$ was the second lowest value, following the concentrations recorded for bottlenose dolphin from Australia. This finding is quite surprising because Zhuhai is situated in the Pearl River Delta and very close to Hong Kong, and thus is expected to be impacted by common pollution sources. Despite this, the total PCB concentration in the Zhuhai sample was some 286 times lower than those of the Hong Kong samples. Although the Zhuhai specimen was considered separately from the Hong Kong samples in the present study, it is conceivable that the Hong Kong and Zhuhai specimens are part of the same Pearl River Delta population. As only one dolphin sample from Zhuhai was measured in this study, and the precise age is unknown, a thorough study involving more specimens will be needed to clarify this point.

It is noted that the concentrations of total DDTs in the Xiamen and Zhuhai samples were comparable with those recorded in stranded dolphins in Hong Kong (Minh et al., 1999). In contrast, concentrations of total DDTs recorded in the stranded dolphin samples from Hong Kong (Minh et al., 1999) were 5-fold higher than those in the biopsy samples (Table 5). This difference may be related

Table 4

Comparison of total PCBs ($\mu g g^{-1}$ we	wet weight) in cetaceans from	Hong Kong with other cetaceans	from different locations in the world
----------------------------------------------	-------------------------------	--------------------------------	---------------------------------------

Comparison of total PCBs (µg g	wet weight) in cetaceans from frong Kong with other cetaceans from different locations in the world					
Species	Locations	Total PCBs ($\mu g g^{-1}$ wet weight)	References			
Bottlenose dolphin	Italian coastal waters	590 (90-1400)	Corsolini et al. (1995)			
Risso's dolphin	Italian coastal waters	320 (20-610)	Corsolini et al. (1995)			
Risso's dolphin	British Columbia coast	1.7	Jarman et al. (1996)			
Bottlenose dolphin	UK	11.1	Wells et al. (1994)			
Bottlenose dolphin	Netherlands	29–41	Koeman et al. (1972)			
Striped dolphin	Western Mediterranean Sea	390 (94–670)	Kannan et al. (1993)			
Bottlenose dolphin	South Atlantic	3.3	De Kock (1989)			
Common dolphin	Northwestern North Pacific	22 (19–26)	Minh et al. (2000)			
Northern right whale dolphin	Northwestern North Pacific	30	Minh et al. (2000)			
Pacific white-sided dolphin	Northwestern North Pacific	27	Minh et al. (2000)			
Bottlenose dolphin	South Africa	14	Cockcroft et al. (1989)			
Bottlenose dolphin	South Africa	nd ^a —10.02	Cockcroft et al. (1991)			
Atlantic spotted dolphin	Florida coast, USA	13 (7.9–19)	Watanabe et al. (2000)			
Bottlenose dolphin	Florida coast, USA	92 (1.6–290)	Watanabe et al. (2000)			
Bottlenose dolphin	East coast USA	180	Geraci (1989)			
Bottlenose dolphin	West coast USA	435	O'Shea et al. (1980)			
Bottlenose dolphin	South China Sea	4.71 (2.15-8.35)	Parsons and Chan (2001)			
Humpback dolphin	Hong Kong	24 (3.3–50)	Minh et al. (1999)			
Humpback dolphin	Hong Kong	20 (5.3-40.8)	Present study			
Humpback dolphin	Xiamen, China	0.25 (0.05-0.5)	Present study			
Humpback dolphin	Zhuhai, China	0.07	Present study			
Fraser's dolphin	Mindanao Sea, Philippines	6.2 (3.8-8.6)	Minh et al. (2000)			
Spinner dolphin	Mindanao Sea, Philippines	2.5 (2.4–2.6)	Minh et al. (2000)			
Fraser's dolphin	Off Kii Peninsula, Japan	51 (45–57)	Minh et al. (2000)			
Striped dolphin	Off Sanriku, Japan	37	Minh et al. (2000)			
Spinner dolphin	Bay of Bengal, India	2.2 (1.6–3.0)	Minh et al. (2000)			
Bottlenose dolphin	India	0.52	Tanabe et al. (1993)			
Bottlenose dolphin	Australia	0.06	Kemper et al. (1994)			

Concentration ranges are shown in parentheses

^a Not detected.

Table 5

Mean concentrations of organochlorine pesticides (ng g^{-1} wet weight) in cetaceans from Hong Kong, Xiamen and Zhuhai

Species	Locations	Total DDTs	HCHs	CHLs	HCB	References
Humpback dolphin	Hong Kong	46,000	760	380	71	Minh et al. (1999)
Humpback dolphin	Hong Kong	9000	1165	259	43	Present study
Humpback dolphin	Xiamen	60,000	228	250	63	Present study
Humpback dolphin	Zhuhai	44,000	33	222	90	Present study

to the distribution of contaminants at different depths of the blubber layer (Krahn et al., 2003). The biopsy tips used in this study were relatively short (to minimize injury to the dolphin), and could only sample the surface blubber layer. Assuming that there is no significant stratification of contaminant concentrations in the blubber, our results would suggest that there may have been a decline in DDT levels in Hong Kong waters. However, further studies will be needed to confirm this.

Amongst the HCH isomers, α -HCH had the lowest detectable concentrations in all the samples measured in this study (Table 2). It is noted that α -HCH is the dominant isomer in technical HCH mixtures. It is conceivable that cetaceans have the ability to metabolize α -HCH effectively (Minh et al., 1999). Indeed, the dominant isomer was found to be β -HCH amongst all the HCH isomers detected in this study. This finding is similar to that found in stranded humpback dolphins in Hong Kong, further suggesting the high resistance of β -HCH against enzymatic degradation (Minh et al., 1999).

This study provides preliminary data on the concentrations of common persistent organic pollutants in the Indo-Pacific humpback dolphins in south China waters, which may contribute to the establishment of a baseline database for a risk assessment of these contaminants in a part of the world that is undergoing unprecedented rapid industrialization.

Acknowledgements

This project was funded by the Hong Kong Research Grants Council (CityU1103/04M). This work was undertaken during tenure of a City University Postgraduate Studentship to CCML. T.A.J. and S.K.H. would like to acknowledge financial support from the Agriculture, Fisheries and Conservation Department, Hong Kong SAR Government. We thank Dr. Charles Sheppard, editor of Marine Pollution Bulletin, for arranging the refereeing of this Baseline paper.

References

- Borrell, A., Aguilar, A., 1990. Loss of organochlorine compounds in the tissues of a decomposing stranded dolphin. Bulletin of Environmental Contamination and Toxicology 45, 46–53.
- Cockcroft, V.G., De Kock, A.C., Lord, D.A., Ross, G.J.B., 1989. Organochlorines in bottlenose dolphins *Tursiops truncatus* from the east coast of South Africa. South African Journal of Marine Science 8, 201–217.

- Cockcroft, V.G., Ross, G.J.B., Connell, A.D., Gardner, B.D., Butler, A.C., 1991. Occurrence of organochlorines in stranded cetaceans and seals from the east coast of southern Africa. In: Leatherwood, S., Donovan, G.P. (Eds.), Cetaceans and Cetacean Research in the Indian Ocean Sanctuary. United Nations Environment Programme, Nairobi, pp. 271–276.
- Corsolini, S., Forcardi, S., Kannan, K., Tanabe, S., Borrell, A., Tatsukawa, R., 1995. Congener profile and toxicity assessment of polychlorinated biphenyls in dolphins, sharks and tuna collected fromItalian coastal waters. Marine Environmental Research 40, 33–53.
- De Kock, A.C., 1989. Chlorinated hydrocarbons as chemical tracers of marine contamination. Ph.D. thesis, University of Port Elizabeth, South Africa.
- Fung, C.N., Lam, J.C.W., Zheng, G.J., Connell, D.W., Monirith, L., Tanabe, S., Richardson, B.J., Lam, P.K.S., 2004. Mussel-based monitoring of trace metal and organic contaminants along the east coast of China using *Perna viridis* and *Mytilus edulis*. Environmental Pollution 127, 203–216.
- Geraci, J.R., 1989. Clinical investigation of the 1987–88 mass mortality of bottlenose dolphins along the US central and south Atlantic coast. Final report to National Marine Fisheries Service and US Navy, Office of Naval Research and Marine Mammal Commission, Washington.
- Hellou, J., Stenson, G., Ni, I.H., Payne, J.F., 1990. Polycyclic aromatic hydrocarbons in muscle tissue of marine mammals from the northwest Atlantic. Marine Pollution Bulletin 21, 469–473.
- Hellou, J., Upshall, C., Ni, H., Payne, J.F., Huang, Y.S., 1991. Polycyclic aromatic hydrocarbons in harp seal (*Phoca groenlandica*) from the northwest Atlantic. Archives of Environmental Contamination and toxicology 21, 135–140.
- Holsbeek, L., Joiris, C.R., Debacker, V., Ali, I.B., Roose, P., Nellissen, J.P., Gobert, S., Bouquegneau, J.M., Bossicart, M., 1999. Heavy metals, organochlorines and polycyclic aromatic hydrocarbons in sperm whales stranded in the southern North Sea during the 1994/1995 winter. Marine Pollution Bulletin 38, 304–313.
- Hung, C.L.H., So, M.K., Connell, D.W., Fung, C.N., Lam, M.H.W., Nicholson, S., Richardson, B.J., Lam, P.K.S., 2004. A preliminary risk assessment of trace elements accumulated in fish to the Indo-Pacific Humpback dolphin (*Sousa chinensis*) in the Northwestern waters of Hong Kong. Chemosphere 56, 643–651.
- Jarman, W.M., Norstrom, R.J., Muir, D.C.G., Rosenberg, B., Simon, M., Baird, R.W., 1996. Level of organochlorine compounds, including PCDDs and PCDFs, in the blubber of cetaceans from the West Coast of North America. Marine Pollution Bulletin 32, 426–436.
- Jefferson, T.A., 2000. Population biology of the Indo-Pacific humpbacked dolphin in Hong Kong waters. Wildlife Monographs 14, 1– 65.
- Kannan, K., Tanabe, S., Borrell, A., Aguilar, A., Focardi, S., Tatsukawa, R., 1993. Isomer-specific analysis and toxic evaluation of polychlorinated biphenyls in stripped dolphin affected by an epizootic in the western Mediterranean Sea. Archives of Environmental contamination and Toxicology 25, 227–233.
- Kemper, C., Gibbs, P., Obendorf, D., Marvanek, S., Lenghaus, G., 1994. A review of heavy metal and organochlorine levels in marine mammals in Australia. The Science of Total Environment 154, 129–139.
- Kennish, M.J., 1996. Practical Handbook of Estuarine and Marine Pollution. CRC Press, Boca Raton, New York (Chapter 4, Polycyclic aromatic hydrocarbons).

- Koeman, J.H., Peeters, W.H.M., Smit, C.J., Tijoe, P.S., Goeij, J.J.M., 1972. Persistent chemicals in marine mammals. TNO-nieuws 27, 570– 578.
- Krahn, M.M., Herman, D.P., Ylitalo, G.M., Sloan, C.A., Burrows, D.G., Hobbs, R.C., Mahoney, B.A., Yanagida, G.K., Calambokidis, J., 2003.
 Blubber stratification in white whales and killer whales: variability in contaminant concentrations, fatty acid profiles, lipid percent and lipid class profiles that has implications for biopsy sampling. International Whaling Commission, Research Paper SC/55/E3.
- Lake, C.A., Lake, J.L., Haebler, R., McKinney, R., Boothman, W.S., Sadove, S.S., 1995. Contaminant levels in harbor seals from the Northeastern United States. Archives of Environmental Contamination and Toxicology 29, 128–134.
- Law, R.J., Whinnett, J.A., 1992. Polycyclic aromatic hydrocarbons in muscle tissue of harbour porpoises (*Phocoena phocoena*) from UK waters. Marine Pollution Bulletin 24 (11), 550–553.
- Marsili, L., Fossi, M.C., Casini, S., Savelli, C., Jimenez, B., Junin, M., Castello, H., 1997. Fingerprint of polycyclic aromatic hydrocarbons in two populations of southern sea lions (*Otaria flavescens*). Chemosphere 34 (4), 759–770.
- Martineau, D., DeGuise, S., Fournier, M., Shugart, L., Girard, C., Lagacé, A., Béland, P., 1994. Pathology and toxicology of Beluga whales from the St. Lawrence Estuary, Quebec, Canada. Past, present and future. The Science of the total Environment 154, 201– 215.
- Minh, T.B., Watanabe, M., Nakata, H., Tanabe, S., Jefferson, T.A., 1999. Contamination by persistent organochlorines in small cetaceans from Hong Kong coastal waters. Marine Pollution Bulletin 39, 383– 392.
- Minh, T.B., Nakata, H., Watanabe, M., Tanabe, S., Miyazaki, N., Jefferson, T.A., Prudente, M., Subramanian, A., 2000. Isomer-specific accumulation and toxic assessment of polychlorinated biphenyls, including coplanar congeners, in cetaceans from the North Pacific and Asian Coastal Waters. Archives of Environmental Contamination and Toxicology 39, 398–410.
- O'Shea, T.J., Brownell, R.L., Clark, D.R., Walker, W.A., Gay, M.L., Lamont, T.G., 1980. Organochlorine pollutants in small cetaceans from the Pacific and South Atlantic oceans, November 1968–June 1976. Pesticides Monitoring Journal 14, 35–46.
- Ou, S.M., Zheng, J.H., Zheng, J.S., Richardson, B.J., Lam, P.K.S., 2004. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons in the

0025-326X/\$ - see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.marpolbul.2005.08.024

surfacial sediments of Xiamen Harbour and Yuan Dan Lake, China. Chemosphere 56, 107–112.

- Parsons, E.C.M., Chan, H.M., 2001. Organochlorines and trace element contamination in bottlenose dolphins (*Tursiops truncatus*) from the South China Sea. Marine Pollution Bulletin 42, 780–786.
- Parsons, E.C.M., Felley, M.L., Porter, L.J., 1995. An annotated checklist of cetaceans recorded from Hong Kong's territorial waters. Asian Marine Biology 12, 79–100.
- Prudente, M., Tanabe, S., Watanbe, M., Subramnian, A., Miyazki, N., Suarez, P., Tatsukawa, R., 1997. Organochlorine contamination in some Odontoceti species from the North Pacific and Indian Ocean. Marine Environmental Research 44, 415–427.
- Pruell, R.J., Quinn, J.G., 1985. Geochemistry of organic contaminants in Narragansett Bay sediments. Estuarine, Coastal and Shelf Science 21, 295–312.
- Richardson, B.J., Zheng, G.J., 1999. Chlorinated hydrocarbon contaminants in Hong Kong surficial sediments. Chemosphere 39, 913–923.
- Tanabe, S., Subramanian, A.N., Ramesh, A., Kumaran, P.L., Miyazaki, N., Tatsukawa, R., 1993. Persistent organochlorine residues in dolphins from the Bay of Bengal, South India. Marine Pollution Bulletin 26, 311–316.
- Watanabe, M., Kannan, K., Takahashi, A., Loganathan, B.G., Odell, D.K., Tanabe, S., Giesy, J.P., 2000. Polychlorinated biphenyls, organochlorine pesticides, tris(4-chlorophenyl)methane and tris(4chlorophenyl)methanol in livers of small cetaceans stranded along Florida coastal waters, USA. Environmental Toxicology and Chemistry 19, 1566–1574.
- Wells, D.E., Campbell, L.A., Ross, H.M., Thompson, P.M., Lockyer, C.H., 1994. Organochlorine residues in harbour porpoise and bottlenose dolphins stranded on the coast of Scotland, 1988–1991. The Science of the Total Environment 151, 77–99.
- Zheng, J., Quinn, J.G., 1988. Analytical procedures to classify organic pollutants in natural waters, sediments and benthic organisms. Acta Oceanologica Sinica 7, 226–236.
- Zheng, G.J., Martin, M., Richardson, B.J., Yu, H., Liu, Y., Zhou, C., Li, J., Hu, G., Lam, M.H.W., Lam, P.K.S., 2004. Concentrations of polybrominated diphenyl ethers (PBDEs) in Pearl River Delta sediments. Marine Pollution Bulletin 49, 520–524.
- Zitko, V., Stenson, G., Hellou, J., 1998. Levels of organochlorine and polycyclic aromatic compounds in harp seal beaters (*Phoca groenlandica*). The Science of the Total Environment 221, 11–29.

Distribution of silver in mussels and oysters along the French coasts: Data from the national monitoring program

Jean-François Chiffoleau *, Dominique Auger, Nathalie Roux, Emmanuelle Rozuel, Anne Santini

IFREMER Centre de Nantes, Departement DCN/BE, BP 21105, 44311 Nantes Cedex 3, France

Distribution and behavior of many trace elements in the aquatic environment has been well characterized, but little

E-mail address: jfchiffo@ifremer.fr (J.-F. Chiffoleau).

is known about silver (Ag) concentrations in coastal waters, even though this element ranks among the most toxic to marine invertebrates (Calabrese et al., 1977; Fisher and Hook, 1997; Webb and Wood, 1998). Studies conducted by Flegal et al. (1995), River-Duarte et al. (1999), and Ndung'u et al. (2001), provided the first valuable data

^{*} Corresponding author. Tel.: +33 (0)2 40 37 41 77; fax: +33 (0)2 40 37 40 75.