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Temporal Trends of Organochlorines and Trace Elements in Marine Mammals from Hong Kong

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Abstract—Temporal trends in the concentrations of organochlorine (OC) compounds and 15 trace elements were examined in Indo-Pacific humpback dolphins (*Sousa chinensis*) and finless porpoises (*Neophocaena phocaenoides*) in Hong Kong. Declining trends were observed in the concentrations of five OC compounds (total chlordanes, total DDTs, endrin, total heptachlors and polychlorinated biphenyls) and Se and Ti in porpoises sampled from 2003–2008. An increasing trend of Se concentrations and a decreasing trend of Zn concentrations were observed in dolphins sampled from 2003–2007. Potential species-specific differences notwithstanding, these findings suggest declining exposure levels of these contaminants in porpoises. However, a previous risk assessment study showed that current levels of DDTs and polychlorinated biphenyls still posed health risks to both cetacean species in Hong Kong, meaning that more continuous monitoring studies are needed.

Keywords: temporal trend, organochlorines, trace elements, cetaceans

INTRODUCTION

South China, including Hong Kong and its neighboring Pearl River Delta (PRD) region, is one of the world's largest economic centers. In recent years, intense economic activities have brought considerable pressure to the marine environment of Hong Kong due to local population growth and industrial development. Hong Kong also receives high volumes of contaminant inputs from the PRD due to its location at the mouth of the Pearl River. Pollutants affecting this area include trace elements (Lam *et al*., 2006; Hung *et al*., 2007), organochlorines (OCs) (Wong *et al*., 2004; Wei *et al*., 2008) and brominated flame retardants (BFRs) (Guo *et al*., 2008; Lam *et al*., 2009), leading to increased concerns about marine water quality and potential impacts on aquatic organisms. In particular, there are two resident cetacean populations in Hong Kong waters, the Indo-Pacific humpback dolphin (*Sousa chinensis*) and finless porpoise (*Neophocaena phocaenoides*). Indo-Pacific humpback dolphins are generally restricted to the northwestern estuarine waters adjacent to the mouth of the Pearl River whereas porpoises are found in the southern and eastern waters, which are largely oceanic and less

subject to pollution stress. Due to their high trophic levels and high body lipid content, these marine mammals are susceptible to exposure to and bioaccumulation of environmental contaminants.

Both cetacean species have been the subjects of previous monitoring studies showing that they accumulate some contaminants to levels that are of concern for their health (Lam, 2007). While continuous monitoring studies have produced data on concentrations of trace elements, OCs and BFRs in these organisms (Ramu *et al.*, 2005, 2006; Isobe *et al.*, 2007; Lam, 2007, 2010; Lam *et al.*, 2009), the temporal trends of these contaminants have not been fully examined. A positive temporal trend in HBCD concentrations has been demonstrated in blubber samples of these cetaceans (Lam *et al.*, 2009). However, a knowledge gap exists for trace elements and OCs. To better understand trends in exposure levels of these contaminants, this paper gathers data on trace element and OC concentrations in samples collected from 2003–2008 in order to conduct preliminary time-series analyses of their levels in the two resident cetacean species in Hong Kong.

MATERIALS AND METHODS

Monitoring datasets from 2003–2007 for the Indo-Pacific humpback dolphin and from 2003–2008 for the finless porpoise were analysed, focusing on concentrations of ten OCs (aldrin, total chlordanes, dieldrin, total dichlorodiphenyltrichoroethanes (total DDTs), endrin, total heptachlors (heptachlor plus heptachlor epoxide), hexachlorobenzene (HCB), mirex, polychlorinated biphenyls (PCBs) and toxaphene) in blubber samples, and of 15 trace elements (Ag, As, Cd, Cu, Co, Cr, Hg, Mn, Mo, Ni, Pb, Sb, Se, Ti and Zn) in liver samples of both cetacean species (Lam, 2007, 2010). To minimize the influence of sex differences caused by maternal transfer and possible age-related differences, adult males with body lengths greater than 200 cm and 120 cm for dolphins and porpoises, respectively, were selected for temporal trend analyses ($n = 1–3$ for each sampling year). Temporal trend analyses were carried out using simple log-linear regression following the procedures described by Nicholson *et al.* (1995). Annual median concentrations were used to perform log-linear regression for the whole monitoring datasets for both species. To investigate possible non-linear trend components, a three-year moving average smoothing function was fitted to the annual median concentrations and was tested by means of ANOVA to see whether it explained significantly more of the variation over time than the log-linear regression model. Statistical analysis was conducted using Prism 5.3 and SigmaStat 3.5. Statistical significance was accepted at $p < 0.05$.

RESULTS AND DISCUSSION

Chemicals showing contrasting temporal trends in the two cetacean species

Of the ten OCs and 15 trace elements, total chlordanes, total DDTs, endrin,

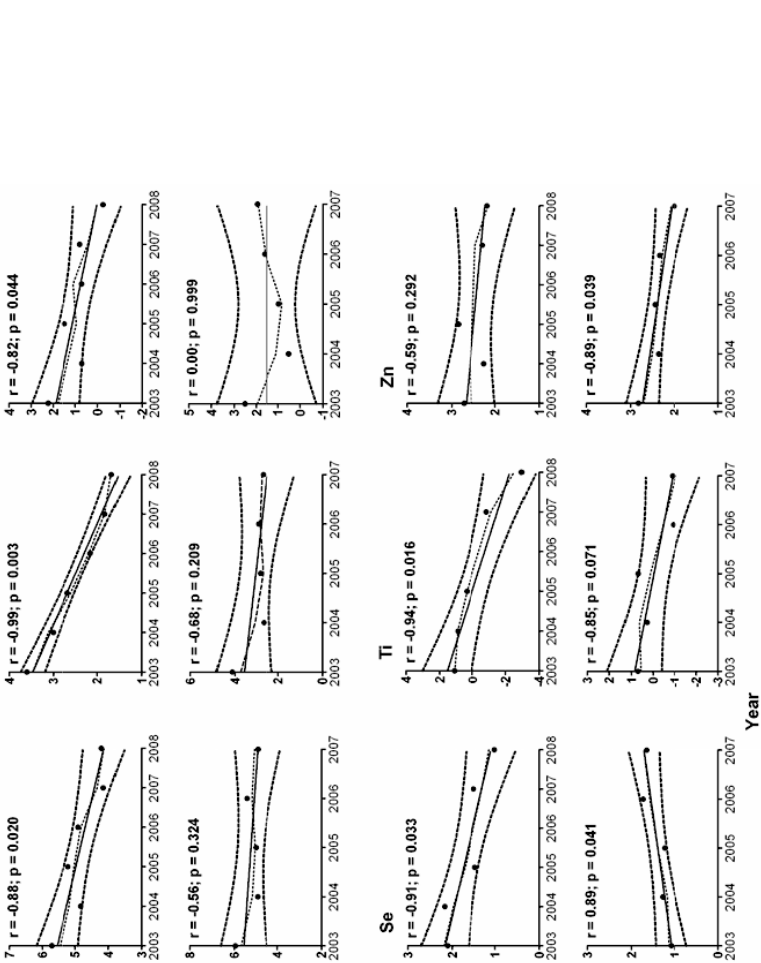

Fig. 1. Temporal trend of concentrations of chemicals showing significant concentration trends in either or both finless porpoises (2003–2008) and Indo-Pacific humpback dolphins (2003–2007) (n = 1–3 individuals per year). Organochlorines (ng/g lipid weight) and trace elements (μg/g dry weight) were quantified in blubber and liver, respectively. Dots and solid lines represent annual median log concentrations and linear regression lines, respectively. Upper and lower dashed lines represent 95% confidence intervals. Broken lines represent three-year moving averages.

total heptachlors, PCBs, Se, Ti and Zn demonstrated differential temporal trends in their concentrations in the finless porpoise and Indo-Pacific humpback dolphin (Fig. 1). Concentrations of total chlordanes showed a negative temporal trend in porpoise samples when log-linear regression analysis of annual median concentrations was used ($r = –0.91$; $p = 0.010$) and dropped by approximately one order of magnitude from 2003 to several hundred ng/g lipid weight (lw) in 2008. In contrast, total chlordane concentrations in dolphins did not vary significantly over time, fluctuating at more or less 10 μg/g lw. Chlordane is banned in Hong Kong but is produced for termite control in mainland China (Wong *et al.*, 2005). The decreasing trend of total chlordanes observed in porpoises but not in dolphins could be due to the lower contaminant exposure levels in the southern and eastern waters of Hong Kong compared to northwestern waters, which are strongly influenced by the runoff from the PRD.

Total DDT concentrations declined linearly with time in the porpoise ($r = –0.88$; $p = 0.020$), showing a 100-fold decrease from 2003 to a level of several ten μg/g in 2008, but no trend was observed in dolphins. The observed decline in porpoises is in agreement with the general declining trend in DDT concentrations after the global ban on its use. However, the small-scale production and use of technical DDT is still permitted in mainland China for mosquito and malaria control (Wong *et al.*, 2005). The presence of DDT as an impurity in dicofol, an acaricide widely in use in China, has been suggested to be a novel source in this region (Guo *et al.*, 2008). Higher proportions of DDT residues than those of its metabolite DDE were observed in dolphins in each year compared to lower proportions in porpoises (Lam, 2007, 2010). Similar proportions have been recorded in biotic matrices from the western waters of Hong Kong (Leung *et al.*, 2005) and the PRD (Guo *et al.*, 2009), indicating fresh DDT inputs into these marine habitats. Although concentrations of total DDTs declined in the porpoise over the time period analysed, health risks due to current exposure levels were found in at least part of the population as well as in dolphins (Lam, 2010), a finding which warrants more continuous monitoring studies.

A negative linear temporal trend was observed in porpoise samples for concentrations of endrin ($r = –0.99$; $p = 0.003$) and total heptachlors ($r = –0.82$; $p = 0.044$), both of which dropped by approximately two orders of magnitude from 2003–2008 to levels of several ng/g lw and several hundred pg/g lw of endrin and total heptachlors, respectively, in 2008. No significant trend for either pesticide was found in the dolphin samples. Concentrations of endrin and total heptachlors in dolphins fluctuated greatly over time, ranging from several ten ng/g lw to several ten μg/g lw and from several ng/g lw to several hundred ng/g lw, respectively. These observations could be the consequence of the lower exposure levels of the two pesticides in the southern and eastern waters of Hong Kong compared to northwestern waters.

Linear regression analysis revealed a negative trend in PCB concentrations in porpoise samples ($r = –0.95$; $p = 0.004$) with an approximately one-order-of-magnitude decrease to several μg/g lw from 2003–2008. Declining PCB concentrations have also been observed in a sediment core sampled from the

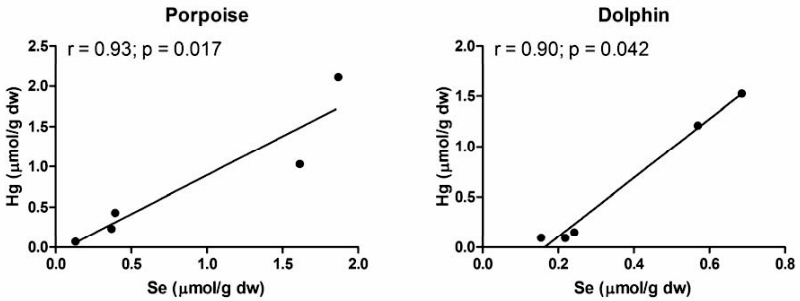

Fig. 2. Pearson correlation between Hg concentrations (μmol/g dw) and Se concentrations (μmol/g dw) in liver samples of finless porpoises and Indo-Pacific humpback dolphins in each corresponding year.

southern waters of Hong Kong that are inhabited by porpoises, agreeing with the fact that the quantity of PCB-containing products used by local industries has dropped significantly (Wei *et al*., 2008). Like DDTs, PCBs were found to pose health risks to a certain portion of both cetacean populations due to their current exposure levels in a recent risk assessment (Lam, 2010). PCBs are no longer used as an industrial chemical in Hong Kong and the disposal of the remaining small number of PCB-containing transformers and capacitors is subject to stringent control measures imposed by the Hong Kong government (EPD, 2006). However, a large proportion of PCB-containing transformers and capacitors remained in use in mainland China long after PCB use was banned in the 1980s (Ramu *et al*., 2006), and PCB contamination of biota from the PRD at ng/g lw – sub – μg/g lw levels has been reported (Nie *et al*., 2005; Wei *et al*., 2008). Dolphins maintained relatively high levels varying between several μg/g lw and several hundred μg/g lw over the sampling period.

Concentrations of Se showed a negative trend in porpoises ($r = -0.91$; $p = 0.033$) and a positive trend in dolphins ($r = 0.89$; $p = 0.041$). Se is believed to be involved in the detoxification of Hg in marine mammals, with levels and uptake of the two elements often being correlated with each other (Parsons, 1999); molar concentrations of Hg correlated well with those of Se in both cetaceans in the present study (Fig. 2), although no statistically significant trends in Hg levels were observed. Molar ratios of Hg:Se in dolphins were generally greater than unity whereas those in porpoises fell below unity. These findings could be the result of Hg sequestration as mercuric selenide in the liver as a means of Hg detoxification in these mammals (Parsons, 1999).

A similar linear decrease in Ti concentrations was found in porpoise samples collected from 2003–2008 ($r = -0.94$; $p = 0.016$), but no significant trend was found in dolphin samples. In contrast, Zn concentrations in dolphin samples decreased linearly from 2003–2007 ($r = -0.89$; $p = 0.039$) but did not show any significant trend in porpoise samples. These observations indicate higher Ti and lower Zn exposure levels in northwestern Hong Kong waters as compared to

southern and eastern waters. Although Ti and Zn are essential in living organisms, their potential toxic effects should not be neglected, especially their size-dependent toxicities. Both elements are components of the new generation of nanomaterials, including TiO_2 and ZnO, and therefore more information on their environmental properties and toxicities is needed in order to carry out a comprehensive risk assessment of these metals in marine cetaceans.

Chemicals showing no significant trend in both cetacean species

Among the five OCs showing no significant trend in both porpoises and dolphins, aldrin and dieldrin have not been used China, including Hong Kong, while toxaphene has been banned in mainland China and Hong Kong for over two decades (Wong *et al.*, 2005). Aldrin concentrations were similar in the two cetaceans, fluctuating below or above 1 ng/g lw. Concentrations of both dieldrin and toxaphene in porpoises varied between several ng/g lw to several hundred ng/g lw, and were generally one order of magnitude lower than those in dolphins. HCB and mirex are banned in Hong Kong but their production is permitted in mainland China for specific applications (Wong *et al.*, 2005). HCB is used as an intermediate for the production of other chlorinated substances and mirex is used as a termiticide (Wong *et al.*, 2005). HCB and mirex persisted in both cetacean species but their levels in porpoises (several ten to several hundred ng/g lw) were generally one order of magnitude lower than those in dolphins (several hundred to several thousand ng/g lw) over the sampling period. High concentrations of OC pesticides have been measured in air and water samples collected from the South China Sea, and it has been suggested that these compounds originate from surrounding developing countries in low-latitude subtropical regions (Zhang *et al.*, 2007). As these five pesticides are highly volatile, atmospheric deposition and other emission sources might contribute to their presence in the marine environment of Hong Kong.

Twelve of the 15 trace elements showed no significant trend in concentrations over time. Trace element contamination has been well documented in sediments from eastern, central and western Hong Kong (Lam, 2007 and references therein). Possible sources of trace elements in Hong Kong waters include industrial pollution, agricultural runoff, vehicle emission, electroplating and textile factories, and ship antifouling paints (Zhou *et al.*, 2007). As economic activities continue, levels of most of these trace elements have remained steady.

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