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Variation in bioaccumulation of persistent organic pollutants based on octanol–air partitioning: Influence of respiratory elimination in marine species

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ABSTRACT

Risk assessments of persistent organic pollutants (POPs) are often based on octanol–water (K_{OW}) partitioning dynamics and may not adequately reflect bioaccumulation in air-breathing organisms. It has been suggested that compounds with low K_{OW} and high octanol–air partitioning (K_{OA}) coefficients have the potential to bioaccumulate in air-breathing organisms, including marine mammals. Here we evaluate differences in concentrations of POPs for two trophically matched Arctic species, spotted seal (*Phoca largha*) and sheefish (*Stenodus leucichthys*). We compared concentrations of 108 POPs in matched tissues (liver and muscle) across three ranges of K_{OW}. We found a significant positive correlation between POP concentration and log K_{OA} in spotted seal tissues for low log K_{OW} compounds (log $K_{OW} < 5.5$, $p < 0.05$). This provides further evidence for empirical models and observed bioaccumulation patterns in air-breathing organisms, and highlights the potential for bioaccumulation of these compounds in Arctic marine mammals.

1. Introduction

Persistent organic pollutants (POPs), including organochlorines (OCs), have been detected in biota in otherwise relatively pristine regions such as the Arctic (AMAP, 2004; Wania and MacKay, 1996). Risks associated with these chemicals depend on their potential for long-range transport, environmental persistence, toxicity, and capacity to biomagnify and bioaccumulate (Letcher et al., 2010; Muir and de Wit, 2010). The Arctic is well recognized as a sink for a number of these persistent, bioaccumulative, and toxic (PBT) chemicals and is of particular interest for POP risk assessments due to their repeated deposition and remobilization (Burkow and Kallenborn, 2000). While international bans on certain industrial POPs have resulted in decreasing trends of some contaminants in Arctic biota since the 1990s, recent studies show that as the Arctic warms due to anthropogenic climate change, contaminants once trapped in ice and permafrost may be released and/or revolitalize (Ma et al., 2011; Moore et al., 2014).

The potential for bioaccumulation and biomagnification of lipophilic contaminants has been repeatedly demonstrated in Arctic environments (Kelly and Gobas, 2003; Muir et al., 1999; Van Oostdam et al., 2005). This is of particular concern in this region where the consumption of the lipid rich tissues of top predators, such as marine fish and mammals, is a vitally important energy source for subsistence populations (Johnson et al., 2009). The fish based food webs of marine mammals result in moderately to highly contaminated tissues of some pinnipeds and cetaceans, including those in Arctic regions (Letcher et al., 2010). Similarly, Arctic subsistence populations are exposed to high quantities of POPs through their diet, which has been associated with adverse health outcomes such as reduced gestation time and impaired fetal development (Dallaire et al., 2013; Laird et al., 2013).

Biomagnification potential is determined by an organism's ability to absorb, biotransform and eliminate a given compound, which is largely dependent upon its physical–chemical properties. The octanol–water (K_{OW}) partition coefficient is often used to assess the tendency for a particular compound to bioconcentrate in the lipid compartments of aquatic organisms (Gossett et al., 1983; Meylan et al., 1999). Understanding and predicting chemical behavior within food webs using quantitative structure activity relationships (QSARs) based on K_{OW} is an important aspect of the registration and management of POPs, and is crucial for identifying potential contaminants of concern. The bioaccumulation models most frequently used to define criteria for acceptable levels of POPs in food, water and sediments have been derived from data collected from aquatic organisms.

Generally, bioaccumulation is considered qualitatively in risk assessments based on a "cut-off" value. For example, in their persistent, bioaccumulative, and toxic (PBT) substance policy statement, the U.S. Environmental Protection Agency (EPA) defines bioaccumulative

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substances as those with a bioconcentration factor (BCF) >1000 (U.S. Environmental Protection Agency, 1999). The European REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) guidelines define a bioaccumulative substance as one with BCF > 2000 (Environment Canada, 1999). If its production volume is <100 tons/year, demonstrating that a chemical has a log K_{OW} < 4.5 (measured or QSAR calculated) can be used in place of BCF data to establish that a compound is not bioaccumulative. The relationship between BCF/BAF and K_{OW} for neutral, lipophilic, organic chemicals has been demonstrated in numerous aquatic and marine food webs in both the laboratory and field (Arnot and Gobas, 2006; Fisk et al., 2001; Russell et al., 1999).

However, using only K_{OW} to predict chemical partitioning under environmental conditions may not adequately reflect actual physical–chemical behavior, particularly in air-breathing species. Compared to aquatic systems, there has been relatively little research assessing the bioaccumulation potential of POPs in terrestrial ecosystems (Gobas et al., 2003; Kelly and Gobas, 2003). QSAR and bioaccumulation models generally do not consider the octanol–air partitioning coefficient (K_{OA}), which may characterize an important excretory route for air-respiring animals including terrestrial vertebrates and marine mammals. The few studies that do incorporate lipid–air partitioning behavior into models of bioaccumulation by terrestrial species or marine mammals suggest K_{OA} may be a better indicator of bioaccumulation potential in air-breathing species (Czub et al., 2008; Kelly et al., 2007; Kelly and Gobas, 2001, 2003).

It has been suggested that compounds with a relatively low K_{OW} (log K_{OW} < 5) can biomagnify in terrestrial food webs (i.e. lichen, wolf and reindeer) for compounds with a relatively high K_{OA} (log K_{OA} > 5) due to low rates of respiratory elimination (Gobas et al., 2003; Kelly and Gobas, 2003). Similarly, it was demonstrated that in a piscivorous marine food web, air-breathing organisms (i.e. marine mammals) display lower concentrations of low K_{OW}, high K_{OA} compounds (e.g. β-hexachlorocyclohexane or β-HCH) than water-respiring organisms at the same trophic position (Kelly et al., 2007). The chemical amplification of compounds with a log K_{OA} > 6 and 2 < log K_{OW} < 5 was estimated to be approximately 2000-fold from base concentrations of primary producers to humans (top predators). This represents a previously underestimated risk to human populations, especially residents of Northern communities that rely on subsistence diets.

Here we present further evidence for the bioaccumulation of low K_{OW}, high K_{OA} compounds in an air-respiring arctic marine mammal relative to a fish species from the same area and trophic level, both of which are important subsistence diet items for the local community. While we cannot account for variation between these two species in exposure to OCs, we have taken several steps including trophic matching, lipid normalization, and PCB 153 normalization in order to eliminate potential confounding variables. Our objective is to compare the concentrations of specific OCs in muscle and liver tissue from both species and assess their relative concentrations as compared to their physical–chemical properties.

2. Methods

2.1. Species selection

Vertebrate OC concentrations are influenced by multiple factors including location, season, year, feeding ecology, tissue and trophic level. We minimized the effects of these variables by carefully selecting study species, spotted seal (*Phoca largha*) and sheefish (*Stenodus leucichthys*), that are spatially, temporally, and trophically matched. Both species are highly piscivorous, occupy similar trophic positions, and were collected in Kotzebue Sound (Alaska) during the winters of 2004–2007. In addition, these species are important subsistence resources for rural communities in northern Alaska.

2.2. Sample collection and storage

Spotted seals were sampled in October of 2004–2007 and sheefish in March 2005 at Kotzebue, AK (66.90°N, 162.59°W) under Marine Mammal Health and Stranding Response Program (MMHSRP) permit #932-1489-07. Blubber, muscle and liver samples from spotted seals (n = 18) and muscle and liver from sheefish (n = 8) were collected for chemical analyses from legally subsistence harvested animals. All animals were assessed for gross general health prior to sampling to allow for data interpretation in the context of animal condition and were deemed to be in excellent physical condition. Collection of samples was performed as previously described (Hoekstra et al., 2002). Samples were immediately frozen at −20 °C, shipped to the University of Alaska Fairbanks (UAF), and stored at −80 °C until analysis.

2.3. Morphometrics and age estimation

Spotted seal and sheefish harvest date, sex, age, and morphometric information appear in Table S1. Seal length was measured as the straight line distance from the tip of the nose to both the base and the tip of the tail. Sheefish length was measured as the straight line distance from the tip of mandible to fork of tail. Seal age was estimated by counting annual growth layers in the cementum of teeth as described by Dehn et al. (2005). Sheefish were aged by counting otolith annual growth increments as described in Brown et al. (2007). Ages were read in triplicate by each of the three independent readers.

2.4. Stable isotopes and trophic level calculations

Nitrogen (N) stable isotope signatures were determined in sheefish and spotted seal muscle and liver. Isotopes were analyzed by the Alaska Stable Isotope Facility using an Elemental Analyzer (Costech Scientific) and a Delta Plus XL Isotope Ratio Mass Spectrometer with a Conflo III interface (Thermo-Finnegan) (EA-IRMS). Each sample was analyzed in duplicate and the mean value was used for all subsequent data analysis. Data are presented in delta notation, where $\delta^{15}N = (R_{sample}\text{-}R_{standard})/(R_{standard})^{*}1000‰$ and R is the ratio of the heavier (^{15}N) to the lighter (^{14}N) isotope and the international standard for N is atmospheric nitrogen (N_{atm}). QA/QC was evaluated via the standard deviations of the reference material, peptone.

Trophic level was estimated for each species using $\delta^{15}N$ based on the following equation:

$$TL = 2 + \left[\left(\delta^{15}N_{consumer}\text{-}\delta^{15}N_{primary\text{-}consumer}\right)/3.8‰\right]$$

where, 2 is the assumed trophic level of the primary consumers of the food web, $\delta^{15}N_{primary\text{-}consumer}$ is 9.8‰ as determined for *Calanus* spp. and 3.8‰ is the trophic enrichment factor for $\delta^{15}N$ in an Arctic marine food web in the Bering Sea of Alaska (Hobson et al., 2002).

2.5. POP analysis

Organochlorines (OCs) were determined in spotted seal and sheefish tissues according to previously described methods (Dietz et al., 2004). Briefly, samples were extracted with dichloromethane (DCM) and quantified using high resolution, single-column capillary gas chromatography with electron capture detection. Standard reference materials (SRM 1588a: organics in cod liver oil) from the National Institutes of Standards and Technology (Gaithersburg, MD, USA) were used to confirm the accuracy and reproducibility of the analytical methods. A calibration check standard was run every six samples, followed by a spike or SRM for quality assurance and control (QA/QC). Method blanks were included to blank correct contaminant concentrations and calculate method detection limits (MDL). The MDL for OCs in tissues varied depending upon analyte and sample size, ranging from

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