

# Probing the Thermodynamics of Biomagnification in Zoo-Housed Polar Bears by Equilibrium Sampling of Dietary and Fecal Samples

Yuhao Chen, Ying Duan Lei, Jaap Wensvoort, Sarra Gourlie, and Frank Wania\*

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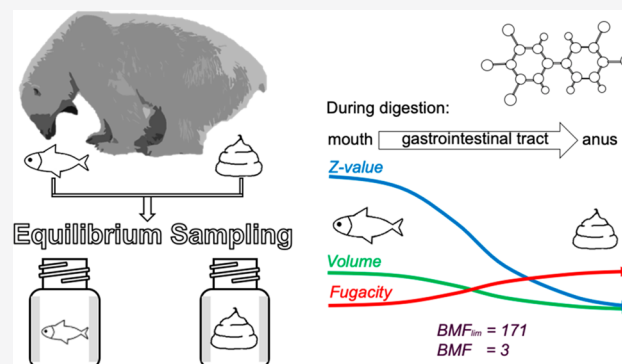
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**ABSTRACT:** In a proof-of-concept study, we recently used equilibrium sampling with silicone films to noninvasively derive the thermodynamic limit to a canine's gastrointestinal biomagnification capability ( $BMF_{lim}$ ) by determining the ratio of the products of the volume ( $V$ ) and fugacity capacity ( $Z$ ) of food and feces. In that earlier study, low contaminant levels prevented the determination of contaminant fugacities ( $f$ ) in food and feces. For zoo-housed polar bears, fed on a lipid-rich diet of fish and seal oil, we were now able to measure the increase in  $f$  of nine native polychlorinated biphenyls (PCBs) upon digestion, providing incontestable proof of the process of gastrointestinal biomagnification. A high average  $BMF_{lim}$  value of  $\sim 171$  for the bears was caused mostly by a remarkable reduction in fugacity capacity driven by a high lipid assimilation capacity. Lipid-rich diets increase the uptake of biomagnifying contaminants in two ways: because they tend to have higher contaminant concentrations and because they lead to a high  $Z$  value drop during digestion. We also confirmed that equilibrium sampling yielded similar  $Z$  values for PCBs originally present in food and feces and for isotopically labeled PCBs spiked onto those samples, which makes the method suitable for investigating the biomagnification capability of organisms, even if native contaminant concentrations in their diet and feces are low.

**KEYWORDS:** Biomagnification, equilibrium sampling, noninvasive, fugacity, fugacity capacity



## INTRODUCTION

Some of the most troublesome contaminants biomagnify in food chains, i.e., achieve higher concentrations in the tissue of a predator than in that of its prey. The potential of a chemical to biomagnify is usually approximated by the ratio of the chemical's lipid-normalized concentrations in the organism and its diet, which is also known as the biomagnification factor (BMF). A biomagnifying chemical's BMF value will exceed unity. Persistent organic pollutants (POPs; e.g., polychlorinated biphenyls, PCBs) with a  $\log K_{OW}$  value ranging between 2 and 9 and a  $\log K_{OA}$  value of above 6 may biomagnify in air-breathing marine and terrestrial mammals.<sup>1</sup> The traditional way to quantify biomagnification is by measuring contaminant concentrations in the tissues of an animal and its diet. This approach is highly invasive and mainly applied to laboratory animals, hunted wildlife, and carcasses, but it is generally not suitable to study biomagnification in endangered species or humans. In an earlier proof-of-concept study,<sup>2</sup> we demonstrated that it is possible to noninvasively derive the thermodynamic limit to a canine's biomagnification capability ( $BMF_{lim}$ ) by determining the ratio of the products of the volumes and  $Z$  values of undigested and digested food.

$$BMF_{lim} = (G_D/G_F)(Z_D/Z_F) \quad (1)$$

Equation 1 shows that quantification of the  $BMF_{lim}$  value involves the determination of the fugacity capacity for biomagnifying contaminants of the diet and feces of an animal (i.e.,  $Z_D$  and  $Z_F$ , respectively) and its volumetric feeding and egestion rates (i.e.,  $G_D$  and  $G_F$ , respectively).<sup>3–5</sup> The  $Z_D$  and  $Z_F$  values can be determined by equilibrating the samples with silicone films and measuring the concentrations in diet and feces ( $C_D$  and  $C_F$ , respectively) and in the silicone in equilibrium with diet and feces ( $C_{siliconeD}$  and  $C_{siliconeF}$ , respectively), as long as the  $Z$  value of silicone for the contaminant ( $Z_{silicone}$ ) is known:

$$Z_{D \text{ or } F} = C_{D \text{ or } F} Z_{silicone} / C_{silicone(D \text{ or } F)} \quad (2)$$

By having the contaminants equilibrate between silicone film and the sample, thereby achieving equal fugacity in either phase, the role of the silicone in that approach is that of a fugacity sensor.<sup>6</sup> In contrast to earlier attempts to sense

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fugacity through measurements in the gas phase,<sup>7,8</sup> the silicone approach is suitable for chemicals in the volatility range of biomagnifying contaminants.

This allows for noninvasive studies on biomagnification in protected species and even in humans. In particular, it should facilitate investigations into how gut physiology, diet, and chemical properties interact in controlling biomagnification. Our results showed that the  $BMF_{lim}$  value is dependent on both the dietary composition (e.g., lipid content,  $P_{lipids}$ ) and the digestion efficiency of a canine.<sup>2</sup> The actual BMF may exceed the  $BMF_{lim}$ , if a chemical is more efficiently absorbed from the intestine than it is lost to the intestine: e.g., as a result of the “fat flush”<sup>9</sup> effect or micelle-mediated transport.<sup>10</sup> The  $BMF_{lim}$  value can also exceed the BMF value, if processes other than fecal elimination notably contribute to the loss of a chemical from the organism.<sup>2</sup>

Another shortcoming of our earlier study was that the original contamination of the diet of the investigated canines was too low to determine the  $Z_D$  and  $Z_F$  values directly.<sup>2</sup> In order to meet the criteria of good equilibrium sampling, the fraction of chemicals extracted by the silicone should be lower than 5%, so that changes in the contaminant levels in the samples due to sampling are negligible.<sup>6</sup> This limits the amount of chemical in the silicone phase, which can cause  $C_{siliconeD}$  and/or  $C_{siliconeF}$  to be too low for reliable quantification, especially if the sample size is small and contaminant levels are low. We circumvented this issue by spiking contaminants on diet and fecal samples in amounts that were high enough for reliable quantification in the silicone while working with sample to silicone ratios that ensured negligible sample depletion.<sup>2</sup> Relying on spiked compounds, however, meant that (i) we had to assume that the measured  $Z$  values of spiked contaminants ( $Z_{spiked}$ ) are similar to the  $Z$  values of contaminants already present in the samples ( $Z_{native}$ ) and (ii) the fugacity of the contaminants in the diet and feces ( $f_D$  and  $f_F$ , respectively) could not be determined. The assumption that  $Z_{spiked} = Z_{native}$  is plausible as long as the spiked compounds are given sufficient time to achieve the same distribution within the samples as the native compound. While this assumption is commonly made,<sup>11</sup> it has not been experimentally confirmed.

The likelihood of succeeding to extract amounts of native contaminants into the silicone phase during equilibrium sampling that are sufficient for reliable quantification can be increased by studying an organism that (i) eats a diet that is naturally contaminated with biomagnifying contaminants and (ii) produces a large amount of feces. This is because equilibrating larger samples with higher contaminant levels will increase the amounts of contaminants in the silicone, without unduly depleting the contaminants in the samples. Polar bears (*Ursus maritimus*) housed at the Toronto Zoo are fed a diet containing sustainably harvested herring, smelt, and seal oil, which contain easily quantifiable levels of some biomagnifying contaminants, such as selected PCB congeners. They also produce copious amounts of fecal matter (~1 L/day). Our hypothesis was that this should make it possible to determine the  $Z$  values of these PCBs originally present in the diet and fecal matter of the bears.

There are other reasons for studying biomagnification in polar bears. Polar bears are one of the world's highest trophic level marine predators. Their seasonal diet, abnormally high in lipids (relying heavily on seal blubber during the period of hyperphagia), yields tissue concentrations of persistent

bioaccumulating compounds, including PCBs, among the highest of any animal in the wild.<sup>12–15</sup> Such elevated concentrations of PCBs may elicit endocrine and immune system disruption in polar bears.<sup>16,17</sup> Of particular concern are effects on the offspring during vulnerable stages of development, since contaminants are able to transfer from mother to cub both *in utero* and during lactation.<sup>18–20</sup> Assessments consistently indicate toxicological risks of PCBs at both the individual and population level.<sup>12,18,21</sup> While the high contamination of polar bears is partially a result of their high trophic level, it is likely also due to their ability to biomagnify contaminants with high efficiency themselves. Earlier studies on biomagnification in polar bears were largely limited to comparing lipid-normalized concentrations of contaminants in hunted bears and their prey.<sup>22–24</sup> These studies found that the BMFs of PCB-99, -138, -153, and -180 were well above 1 for wild polar bears (ranging from 2 to ~50), while the BMFs of PCB-52 and -101 for polar bears in the central East Greenland region were close to 1, probably because the bears are capable of metabolizing these PCB congeners.<sup>24,25</sup> Usually, adult females have lower BMF values than male bears since they can transfer contaminants to their offspring.<sup>19,22</sup>

If it is possible to determine the  $Z$  values of contaminants originally present in diet and feces (i.e.,  $Z_{D or F}$ ), it should further be possible to calculate the fugacity of the contaminants in those phases using

$$f_{D or F} = C_{D or F} / Z_{D or F} \quad (3)$$

Comparing the fugacity in diet and feces would then allow for confirmation of the main principle of gastrointestinal biomagnification, which stipulates that the increase in the fugacity of biomagnifying contaminants in the gut content provides the thermodynamic driving force for the diffusive uptake of those contaminants from the gut.<sup>3,4</sup>

Being able to measure the  $Z$  values for contaminants originally present in food and feces ( $Z_{native}$ ) further would allow us to test whether native and spiked contaminants have indeed the same  $Z$  values in a sample. Specifically, we could add isotopically labeled versions of the originally present contaminants to the same samples and determine their  $Z$  values alongside those of the native contaminants.

Here we show that it is possible to measure the  $Z$  values and the fugacities or activities of PCB congeners (i.e., PCB-28, -44, -52, -99, -101, -118, -138, -153, and -180) originally present in the diet and feces of zoo-housed polar bears, thereby providing a comprehensive picture of the thermodynamics of biomagnification in an organism in a completely noninvasive manner. We further demonstrate that native and spiked PCBs have similar  $Z$  values in dietary samples.

## ■ MATERIALS AND METHODS

**Laboratory Materials.** Details about deuterated standards and other chemicals are given in Table S1 in the Supporting Information.

**Sample Collection and Preparation.** Paired diets and feces of zoo-housed polar bears (*Ursus maritimus*, three females: two 20-year-old adults and a 5-year-old subadult) were collected in November 2019. Because the fecal samples could not be assigned to any particular polar bear, the three bears were considered as a collective. The dietary items included horse meat, herring, smelt, seal oil, and various vegetables. All samples were wrapped in baked aluminum foil

and stored in sealed plastic bags at  $-20\text{ }^{\circ}\text{C}$  until analysis. The dietary intake rate,  $G_D$  (in unit of g/day), of the polar bears was estimated from the amount of food provided to the bears, whereas the egestion rate  $G_F$  was estimated from the average body weight of the bears using an empirical relationship by Yang et al.<sup>26</sup> Whereas it would have been preferable to measure  $G_F$ , the quantitative collection of fecal matter for individual bears within the zoo's joint enclosure was not possible. Densities of dietary and fecal samples ( $\rho_{D\text{ or }F}$ ), quantified by immersing a preweighed sample into a water-filled vial,<sup>2</sup> were used to obtain  $G_D$  and  $G_F$  in units of mL/day (Table S3).

Details of the sample preparation are given in Text S1 in the Supporting Information. To create a spiked sample puree, around 350 g of dietary samples (with addition of up to 40% water) were homogenized into a smooth puree using a blender. After 6 g of a bioinhibitor (i.e., sodium azide) was added to prevent decomposition of the sample during the experiments,<sup>27</sup> and after six deuterated standards (i.e.,  $^{13}\text{C}_{12}$ -PCB-28, -52, -101, -138, -153, and -180) were added, the sample puree was allowed to rotate on a roller mixer at 10 rpm for 2 days. Because of their large mass and the limited capacity of the blender, fecal samples were first homogenized in batches (with addition of up to 41% water), combined with  $\sim 25$  g of sodium azide in a 4 L beaker, and fully mixed with a solvent-cleaned metal rod. No chemicals were spiked onto fecal samples. Approximately 30–45 g of homogenized dietary and fecal sample puree was collected for the determination of native and/or labeled PCB concentrations (Table S4).

**Passive Equilibrium Sampling.** Dietary samples were equilibrated with silicone films in glass vials (40 mL, VWR International Canada, Mississauga, ON), whereas larger glass jars (500 mL, Uline Canada, Milton, ON) were used for fecal samples. Larger vessels are required for the latter because the low contaminant levels necessitate a large sample volume. The inner walls of the glass vessels were coated with Dow Corning 1-2577 silicone polymer (EMD Chemicals Inc., Mississauga, ON) using a procedure described in detail in Text S2. The amount of silicone was chosen to achieve nominal film thicknesses of 6, 12, 16, 18, and 20  $\mu\text{m}$  for vials or 0.4, 0.8, and 1.5  $\mu\text{m}$  for jars. The actual mass of silicone film was recorded gravimetrically for each individual vessel.

Details of the procedure used to equilibrate the samples with the silicone are given in Text S3.<sup>2</sup> Briefly, approximately 35 g of the dietary sample was transferred into a silicone-coated vial and allowed to equilibrate on a roller mixer at 10 rpm for up to 5 days. Similarly, 350 g of fecal matter was transferred into a jar and equilibrated for 2 weeks on a roller mixer. Blanks were treated similarly but contained only the sodium azide solution. Duplicates for each film thickness meant that 10 vials and 6 jars were equilibrated with samples. After equilibration, samples were removed from the vessels, and any residue was rinsed with deionized (DI) water and wiped with clean lint-free tissues. After rinsing, each silicone-coated vial was reweighed in order to quantify any residual lipid mass in the vials. The chemicals absorbed by the silicone polymer were extracted three times with 8 mL of hexane for 90 min, and the combined extracts were purified by silica gel columns prior to analysis.

**Chemical Analysis.** The PCB concentrations in homogenized food and feces samples ( $C_{D\text{ or }F}$ ) and in silicone extracts ( $C_{\text{silicone}(D\text{ or }F)}$ ) were quantified by GC-MS/MS as described previously.<sup>28</sup>

**Data Analysis.** The assimilation efficiency of food for polar bears ( $AE_{\text{food}}$ ) could be determined by the ratio of the egestion rate ( $G_F$ ) and feeding rate ( $G_D$ )

$$AE_{\text{food}} = 1 - G_F/G_D \quad (4)$$

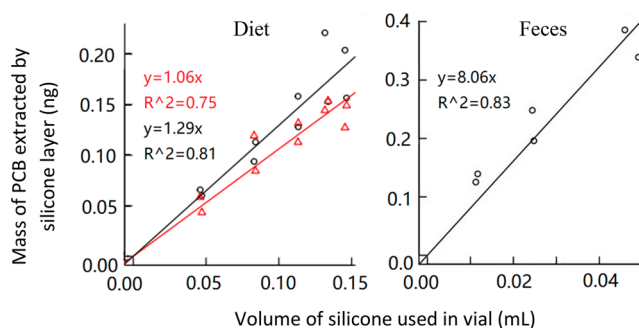
Using the measured lipid content of diet and feces ( $P_{\text{lipids }D\text{ or }F}$ ), we further calculated the assimilation efficiency of lipids ( $AE_{\text{lipids}}$ )

$$AE_{\text{lipids}} = 1 - (P_{\text{lipids }F}G_F)/(P_{\text{lipids }D}G_D) \quad (5)$$

The uptake efficiency of PCBs ( $E_{\text{PCBs}}$ ) is calculated using

$$E_{\text{PCBs}} = 1 - (C_F G_F)/(C_D G_D) \quad (6)$$

The mass of a PCB quantified in the silicone was plotted against the volume of silicone in a vessel (calculated from its mass and a density of 1.1 g/mL) (Figure 1). For silicone



**Figure 1.** Plot of the amount of native (black, O) and/or labeled (red,  $\Delta$ ) PCB-153 quantified in silicone layers with dietary (left) and fecal (right) samples against the volume of those silicone layers. A linear relationship indicates that equilibrium was achieved, and the slope of the relationship yields the concentration in the silicone (in units of ng/mL).

equilibrated with a lipid-rich diet, the PCB mass was first reduced by the mass of PCBs in a residual lipid layer coating the silicone film.<sup>2</sup> A straight line through the origin indicates that equilibrium was established.<sup>29</sup> The slope of the regression line yields the PCB concentrations in the silicone ( $C_{\text{silicone}}$ ) (Figure S1).

The fugacity  $f$  of a chemical in two phases in chemical equilibrium is the same:

$$f_{\text{silicone}} = f_{D\text{ or }F} \quad (7)$$

Because  $f$  is the ratio between the concentration and fugacity capacity of a chemical in a phase

$$f_{\text{silicone}} = C_{\text{silicone}(D\text{ or }F)}/Z_{\text{silicone}} = C_{D\text{ or }F}/Z_{D\text{ or }F} = f_{D\text{ or }F} \quad (8)$$

We therefore can calculate the fugacity of diet or feces using the concentration and  $Z$  value in silicone

$$f_{D\text{ or }F} = C_{\text{silicone}(D\text{ or }F)}/Z_{\text{silicone}} \quad (9)$$

where  $Z_{\text{silicone}}$  was calculated using Henry's law constants ( $H$ ) and partitioning ratios between silicone and water ( $K_{\text{silicone}/W}$ ) reported for PCB congeners in ref 30

$$Z_{\text{silicone}} = K_{\text{silicone}/W}/H \quad (10)$$

By dividing the fugacity by the saturation vapor pressure of the subcooled liquid ( $P_L^S$ )<sup>31,32</sup> at the same temperature as the temperature at which the fugacity was measured (i.e.,  $23\text{ }^{\circ}\text{C}$ ),

we can also calculate the chemical activity of the PCBs in diet and feces ( $\alpha_{D \text{ or } F}$ ):<sup>33</sup>

$$\alpha_{D \text{ or } F} = f_{D \text{ or } F} / P_L^S \quad (11)$$

The fugacity capacity of diet or feces is obtained by dividing the concentration in the biological phase by the fugacity in that phase:

$$Z_{D \text{ or } F} = C_{D \text{ or } F} / f_{D \text{ or } F} \quad (12)$$

The relative contributions of lipids ( $\phi_{\text{lipids}}$ ) and nonlipid organic matter (NLOM) ( $\phi_{\text{NLOM}}$ ) to the bulk  $Z$  values are determined as<sup>2</sup>

$$\phi_{\text{lipids}} = (V_{\text{lipids}} / V_{D \text{ or } F} Z_{\text{lipids}}) / Z_{D \text{ or } F} \quad (13)$$

$$\phi_{\text{NLOM}} = 1 - \phi_{\text{lipids}} \quad (14)$$

where  $V_{\text{lipids}}$  and  $V_{D \text{ or } F}$  were the volume of lipids and diet (or feces), respectively.  $Z_{\text{lipids}}$  was estimated as the ratio of the partitioning ratio between storage lipids and water ( $K_{\text{storage-lipids/W}}$ )<sup>34</sup> and  $H$ :<sup>31,35</sup>

$$Z_{\text{lipids}} = K_{\text{storage-lipids/W}} / H \quad (15)$$

Finally, the  $\text{BMF}_{\text{lim}}$  value is calculated by combining eqs 1 and 2:<sup>2</sup>

$$\text{BMF}_{\text{lim}} = [(C_D C_{\text{siliconeF}}) / (C_F C_{\text{siliconeD}})] (G_D / G_F) \quad (16)$$

Except for extremely hydrophobic organic contaminants, the kinetics of transport across the gut wall is sufficiently fast relative to the residence time of digested matter within the intestine for equilibrium between the bear's tissues and the digested food to be approached. During a laboratory study on rainbow trout, Gobas et al. observed that "lipid-based concentrations of PCBs in the fish were comparable to lipid-based concentrations in the intestinal content, indicating that fish and intestinal content were close to a chemical equilibrium".<sup>36</sup> If we therefore assume the feces to be in chemical equilibrium with the bears' tissues ( $f_B = f_F$ ), we can calculate the BMF as a ratio of two fugacities:

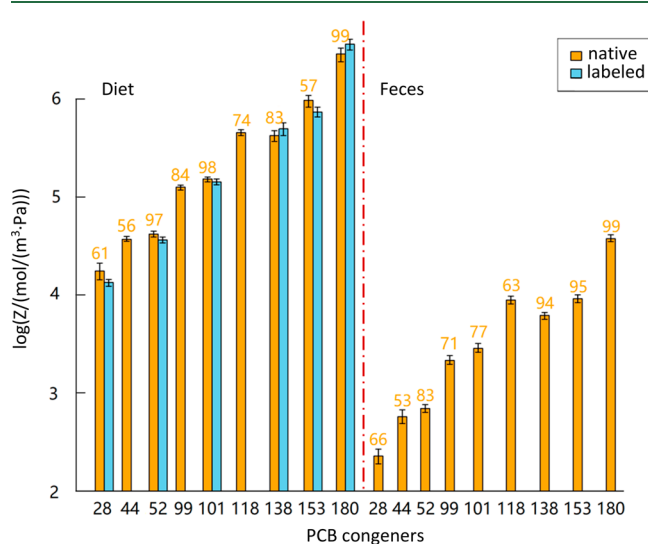
$$\text{BMF} = f_F / f_D \quad (17)$$

## RESULTS AND DISCUSSION

**Assimilation and Uptake Efficiency for Food, Lipids, and PCBs.** Zoo-housed polar bears with an average body weight of 303 kg consumed  $\sim 2.3 \text{ L day}^{-1}$  of food (including horse meat, herring, smelt, seal oil, and various vegetables) (Table S3). The food assimilation efficiency was  $\sim 60\%$ , resulting in approximately  $0.96 \text{ L day}^{-1}$  of fecal matter egestion, presumably indigestible fiber and/or protein. The polar bears reduced the lipid content in their diet from 24.1% to 0.3% during digestion, thus resulting in an assimilation efficiency of lipids of 99%. On the basis of the measured total dietary PCB concentration ( $C_{\Sigma \text{PCBs}} = 20 \text{ ng/mL}$ ), the daily uptake of nine major native PCB congeners by the bears was  $46.7 \mu\text{g day}^{-1}$ . Seal oil and herring accounted for 61% and 31% of the dietary PCB uptake, respectively, with smelt and horse meat making only minor contributions of 8% and 0.2%, respectively (Figure S3). This daily uptake of PCBs for zoo-housed polar bears is likely much lower than that for most polar bears in the wild, because the latter ingest much more Arctic ringed seal (*Phoca hispida*) blubber ( $\sim 740 \text{ g day}^{-1}$  on average) than the zoo-housed bears ingest seal oil ( $\sim 180 \text{ g}$

$\text{day}^{-1}$ ).<sup>37,38</sup> Also, concentrations of PCBs reported in Arctic ringed seal are comparable to, if not higher than, concentrations in the seal oil fed to the zoo-housed bears.<sup>22,39</sup> As only  $0.8 \mu\text{g day}^{-1}$  of PCBs was eliminated through fecal egestion, more than 98% of the PCBs were taken up in the bears' body or biotransformed.<sup>40</sup> This value easily outcompetes the uptake efficiency of PCBs for fish ( $\sim 40\%$ )<sup>41–43</sup> and is comparable to that for other mammals: e.g., humans ( $>80\%$ )<sup>44</sup> and gray seal (*Halichoerus grypus*,  $\sim 96\%$ ).<sup>45</sup>

**Dietary and Fecal Fugacity Capacities.** The measured fugacity capacities of dietary and fecal samples for the PCBs are shown in Figure 2 and Table S6. In both types of samples, the

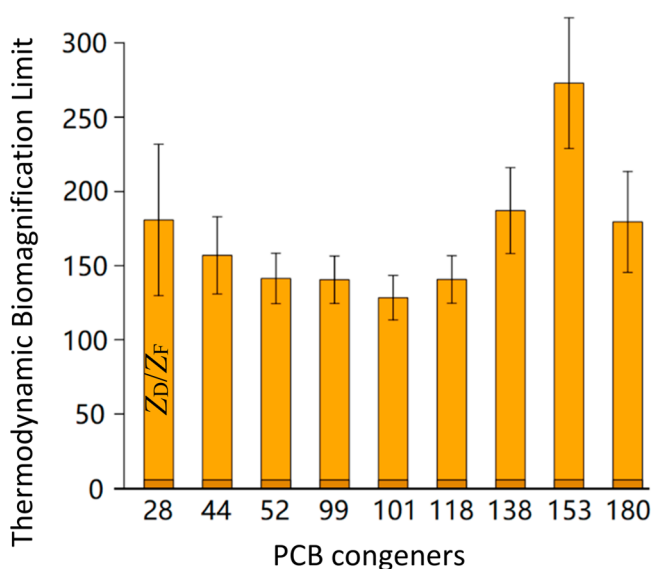


**Figure 2.** Logarithm of the fugacity capacity of selected PCB congeners in the diet ( $Z_D$ , left) and feces ( $Z_F$ , right) of polar bears. The  $Z_D$  values of six isotopically labeled PCBs spiked onto the dietary samples are also shown (blue bars). The numbers above a bar indicate the contribution of lipids to the bulk  $Z$  value in percent.

measured  $Z$  values of the PCBs increase with a congener's degree of chlorination, i.e., with increasing hydrophobicity. For example, the dietary and fecal  $Z$  values for PCB-180 exceed those for PCB-28 by 2 orders of magnitude. The average contributions that lipids make to the bulk  $Z$  values of the PCBs were estimated to be  $79 \pm 18\%$  and  $78 \pm 16\%$  for dietary and fecal samples, respectively (Table S10). While lipids are thus the major contributor to the bulk  $Z$  values, nonlipid organic matter (NLOM), such as protein, still contributed notably (on average 21% and 22% for diet and feces, respectively). It should therefore be possible to obtain a rough estimate of the  $Z$  values of a biological sample for PCBs on the basis of its lipid content alone. For example, the polar bear diet with a  $P_{\text{lipids}}$  value of 24% has a  $Z$  value for PCB-153 ( $Z_{D, \text{PCB153}} = (9.7 \pm 1.3) \times 10^5 \text{ mol Pa}^{-1} \text{ m}^{-3}$ ) that is 1 order of magnitude higher than that previously measured for the diet of zoo-housed Arctic wolves having a  $P_{\text{lipids}}$  value of 2% ( $Z_{D, \text{PCB153}} = (8.7 \pm 1.3) \times 10^4 \text{ mol Pa}^{-1} \text{ m}^{-3}$ ).<sup>2</sup> However, information on NLOM (e.g., characterization of NLOM and their physical properties and volume percentages in a sample) is still necessary to obtain an accurate estimate of bulk  $Z$  value. The carbon content of polar bear feces was 12% ww, which was less than half of the carbon content of the feces of a domestic dog (juvenile dog, 34%; adult dog, 28%) and wolf (54%). However, the  $\phi_{\text{NLOM}}$  in bear feces had a value (22%) similar to that of the previously

measured  $\phi_{\text{NLOM}}$  in adult dog feces (20%), even though it was still much lower than that in juvenile dog (40%) and wolf feces (75%).<sup>2</sup> Obviously, the carbon content alone cannot fully explain the  $\phi_{\text{NLOM}}$  value in a fecal sample, and the characterization of NLOM is crucial. The low  $\phi_{\text{NLOM}}$  in both polar bear and adult dog feces might be due to a large portion of indigestible fibers with a low absorptive capacity for HOCs, e.g., from fresh fruit (e.g., apple) and vegetables (e.g., potato).

**Thermodynamic Biomagnification Limit.** The ratio between dietary and fecal fugacity capacity (i.e.,  $Z_{\text{D}}/Z_{\text{F}}$ ) for the different PCB congeners averaged  $71 \pm 18$ . When this is combined with a ratio of feeding and egestion rates ( $G_{\text{D}}/G_{\text{F}}$ ) of 2.4, we estimate a  $\text{BMF}_{\text{lim}}$  value of  $171 \pm 45$  for zoo-housed polar bears. Whereas  $G_{\text{D}}$  is known with high precision, the uncertainty of the estimated  $G_{\text{F}}$  will add some uncertainty to the  $\text{BMF}_{\text{lim}}$  value. The  $\text{BMF}_{\text{lim}}$  values for individual PCBs are shown in Figure 3 and Table S6.  $Z_{\text{D}}/Z_{\text{F}}$  and therefore also



**Figure 3.** Thermodynamic biomagnification limit ( $\text{BMF}_{\text{lim}}$ ) in polar bear. The measured  $\text{BMF}_{\text{lim}}$  includes two quotients: the quotient of the  $G$  values ( $G_{\text{D}}/G_{\text{F}}$ ) and the quotient of the  $Z$  values ( $Z_{\text{D}}/Z_{\text{F}}$ ). The greyer lower section of the bars indicates the relative contribution of  $G_{\text{D}}/G_{\text{F}}$ , whereas the lighter upper section designates the contribution of  $Z_{\text{D}}/Z_{\text{F}}$ .

$\text{BMF}_{\text{lim}}$  are not very variable between different congeners (Table S6). In particular, there is no clear trend with hydrophobicity: i.e., the trends for the  $Z_{\text{D}}$  and  $Z_{\text{F}}$  values cancel each other out. The values indicate that the digestion of food by the bears is so efficient that it can decrease the diet's capacity to accommodate PCBs by almost 2 orders of magnitude. This is a combined effect of the high dietary lipid content of 24% and the very high lipid absorption efficiency of 99%. The dietary volume reduction makes a relatively limited contribution to the  $\text{BMF}_{\text{lim}}$  value of PCBs in polar bears mostly because the relationship by Yang et al.<sup>26</sup> indicates that the food adsorption efficiency decreases with an organism's body size. Gobas et al. recently used simple simulations to illustrate how a high lipid content in a diet leads to high  $\text{BMF}$  values by allowing for a larger decrease in the  $Z$  value of the diet during digestion.<sup>46</sup>

Remarkably, we can infer that the  $\text{BMF}_{\text{lim}}$  value of PCBs in wild polar bears is even higher, because their diet is likely to

have an even higher lipid content,<sup>38</sup> whereas there is little reason to expect the lipid absorption efficiency to be lower in wild bears than in zoo-housed bears. For illustration, for a bear feeding exclusively on ringed seal blubber (dietary lipid content of 98%) and having the same lipid assimilation efficiency as the zoo bears (99%), we can estimate a  $\text{BMF}_{\text{lim}}$  value as high as 10000.

**Dietary and Fecal Fugacity.** By conducting our measurements with the PCBs originally present in the bears' diet and feces, we could determine the fugacities of the PCBs in those samples using eq 3. They range from  $\sim 5 \times 10^{-7}$  Pa for PCB-180 in the diet to  $\sim 1 \times 10^{-4}$  Pa for PCB-52 in feces (Table S7). The "effective concentration" or chemical activity of native PCB congeners ranged from  $(8.44 \pm 0.14) \times 10^{-4}$  for PCB-28 in diet to  $(8.81 \pm 0.54) \times 10^{-2}$  for PCB-138 in feces (Table S8). Chemical activities in all samples were well below 1, which indicated that the contaminants were far from saturation in the samples. The ratio of fecal and dietary fugacities ( $f_{\text{F}}/f_{\text{D}}$ ) or activities ( $a_{\text{F}}/a_{\text{D}}$ ) were always above 1 and averaged  $2.8 \pm 1.5$  (Table S7): i.e., the fugacities or activities of the PCBs in the gut content increased upon digestion. It is this increase in fugacity or activity that provides the driving force for the transfer of PCBs moving from the bear's gut to its tissues. Gobas et al. had previously observed an increase in the fugacity upon digestion by measuring the change in the lipid normalized concentration of a PCB congener in the diet and the contents of the stomach and four intestinal sections of a rainbow trout.<sup>36</sup> We believe that this is the first experimental confirmation of the process of gastrointestinal biomagnification in a mammal. Importantly, this could be done noninvasively, without requiring the feeding of deliberately contaminated food and without relying on the assumption that lipid-normalized concentrations are a good surrogate for fugacity.

The  $\text{BMF}$  value, when it is defined as the fugacity ratio between fecal matter and the undigested food (i.e.,  $f_{\text{F}}/f_{\text{D}}$ ), equals  $2.8 \pm 1.5$ . That this  $\text{BMF}$  value is much smaller than the  $\text{BMF}_{\text{lim}}$  value indicates that the uptake and elimination of PCBs in the polar bears are far from a steady state: i.e., the bear would need to take up much more PCBs for the rate of elimination to equal the rate of uptake. This is also supported by the almost complete uptake of PCBs (98%) from the food, including of congeners known to biotransform very slowly. At the steady state, there would be no net chemical transfer between the bear's gut content and body tissues. In that situation, we would expect the fugacity of the food to rise dramatically during digestion, and the  $f_{\text{F}}/f_{\text{D}}$  or  $\text{BMF}$  value would eventually equal the  $\text{BMF}_{\text{lim}}$  value.

A simple mass balance calculation can yield the time ( $t$ ) that would be required to allow uptake and elimination of PCBs in polar bears to reach a steady state. Using PCB-153 (with a molecular weight,  $\text{MW}_{\text{PCB153}}$ , of 360.9 g/mol) as an example

$$t = m_{\text{bear at SS}} / (C_{\text{D}} G_{\text{D}} E_{\text{PCBs}}) \quad (18)$$

where the  $m_{\text{bear at SS}}$  value is the mass of PCB-153 that would be required to bring the fugacity in the bear up to the fugacity in the bear's feces (i.e., to reach steady state) and could be calculated as

$$m_{\text{bear at SS}} = V_{\text{bear}} Z_{\text{bear}} f_{\text{F}} \text{MW}_{\text{PCB153}} \quad (19)$$

Here, we apply the PCB absorption efficiency, body weight, dietary intake rate, and dietary contamination of the zoo bears throughout their lifespan. The volume of a bear ( $V_{\text{bear}}$ ) and its

organs are shown in Table S11. The  $Z_{\text{bear}}$  value was estimated based on the lipid content in the bear's organs. We estimated that a bear would need to take up more than 400 g of PCB-153 to reach a steady state and that steady state would never even be remotely approached within the lifespan of a bear (~30 years) (Table S11). This time will be even longer if we also consider the decrease in the uptake efficiency of PCB-153 as the fugacity in the bears approaches a steady state.

The ratio between lipid-normalized concentrations of PCBs in feces and diet ( $C_{\text{F}}/C_{\text{D}}$ ) is  $2.9 \pm 0.8$  on average (Table S7) and is essentially identical with the fugacity ratio ( $f_{\text{F}}/f_{\text{D}} = 2.8 \pm 1.5$ ) we measured. This equality is quite remarkable, and not entirely expected, considering the huge difference in the lipid content of diet and feces. This provides support for estimating BMF as the ratio of lipid-normalized concentrations of lipophilic contaminants<sup>47</sup> in diet and feces when measurements of fugacity are not feasible. However, without an equilibrium sampling approach, no detailed insight into the thermodynamics of the biomagnification process can be gained as neither fugacities nor  $Z$  values could be obtained. Furthermore, it still should be confirmed that ratios of lipid-normalized concentrations in feces and diet consistently give reliable estimates of the ratio of the fugacities in those two phases.

#### Comparison of $Z$ Values for Spiked and Native PCBs.

The measured  $Z$  values of native and labeled PCB congeners were not significantly different ( $p$  values  $>0.05$ ; fail to reject the null hypothesis) (Figure 2 and Table S9). This is dependent on the assumption that the  $Z$  values of the silicone polymer for native and labeled compounds is the same ( $Z_{\text{silicone\_native}} = Z_{\text{silicone\_labeled}}$ ), which is very plausible. In other words, the PCBs originally present in the samples and those spiked onto the dietary samples behave similarly in our measurements: i.e., partition between the dietary samples and the silicone in a similar manner. This implies that one is not reliant on the contaminants originally present in a biological sample to determine the sample's fugacity capacity for those contaminants and therefore provides support for an approach using spiked samples, as advocated in our earlier study.<sup>2</sup>

By showing that equilibrium sampling yields similar  $Z$  values for contaminants originally present in food and feces and for their isotopically labeled versions spiked onto those samples (i.e.,  $Z_{\text{native}} \approx Z_{\text{labeled}}$ ), it becomes further possible to determine the fugacity of native contaminants even in samples with a concentration of native contaminants  $C_{\text{native}}$  too low to determine the  $Z_{\text{native}}$  value, using

$$f_{\text{native}} = C_{\text{native}}/Z_{\text{spiked}} \quad (20)$$

This requires only that (i)  $C_{\text{native}}$  is high enough to be reliably quantified and (ii) the sample size is sufficiently large to be able to determine the  $Z$  value for spiked compounds using the equilibrium sampling approach. Importantly, these spiked compounds do not have to be isotopically labeled.

**Comparison with Other Species.** Combining the ratio between dietary and fecal fugacity capacities (i.e.,  $Z_{\text{D}}/Z_{\text{F}}$ ) for the polar bear of  $71 \pm 18$  with a  $G_{\text{D}}/G_{\text{F}}$  value of 2.4, we estimate an average  $\text{BMF}_{\text{lim}}$  value for PCBs in polar bears of ~171. The BMF value (i.e.,  $f_{\text{F}}/f_{\text{D}}$ ) in polar bears was only  $2.8 \pm 1.5$ , since the uptake and elimination of PCBs in the polar bears were far from a steady state.

The  $Z_{\text{D}}/Z_{\text{F}}$  values of all previous study objects (Arctic wolf, 3; juvenile dog, 9; adult dog, 20) were much lower than those for polar bears.<sup>2</sup> Even though the  $G_{\text{D}}/G_{\text{F}}$  values for the canines

(Arctic wolf, 15; juvenile dog, 3.7; adult dog, 4.0) were higher than that for polar bears, the  $\text{BMF}_{\text{lim}}$  values of PCBs in canines (Arctic wolves, 41, juvenile dog, 35; adult dogs, 81)<sup>2</sup> were still considerably lower than that of the bears. Using eq 20, we can calculate the fugacity of PCBs in the dietary and fecal samples for canines from our earlier study. Using these data, we estimated  $f_{\text{F}}/f_{\text{D}}$  ratios of  $1.3 \pm 0.3$  for an Arctic wolf. The  $f_{\text{F}}/f_{\text{D}}$  ratio for a domestic dog was not available, since  $C_{\text{native}}$  was below the detection limit and could not be quantified reliably.

Consequently, the zoo-housed polar bears had a high biomagnification capability in comparison to zoo-housed Arctic wolves and domestic dogs. This was due to (i) a high dietary lipid content ( $P_{\text{lipids\_polar\_bear}} = 24.1\%$  in comparison with  $P_{\text{lipids\_Arctic\_wolf}} = 2.2\%$ ,  $P_{\text{lipids\_juvenile\_dog}} = 7.7\%$ , and  $P_{\text{lipids\_adult\_dog}} = 6.7\%$ ) elevating the  $Z_{\text{D}}$  value, (ii) a high digestion efficiency for lipids ( $\text{AE}_{\text{lipids\_polar\_bear}} > 99\%$  in comparison with  $\text{AE}_{\text{lipids\_Arctic\_wolf}} = 98.3\%$ ,  $\text{AE}_{\text{lipids\_juvenile\_dog}} = 96.9\%$ , and  $\text{AE}_{\text{lipids\_adult\_dog}} = 98.0\%$ ) lowering the  $Z$  value in feces, (iii) relatively contaminated diets leading to a high  $f_{\text{D}}$  value, and (iv) a high uptake efficiency of contaminants, resulting a small  $C_{\text{F}}$  value and further a low  $f_{\text{F}}$  value.

The example of the polar bear illustrates why a high-lipid diet is doubly problematic for the uptake of hydrophobic contaminants. On the one hand, a high-lipid diet is more likely to contain higher levels of such contaminants, especially if these lipids are derived from animals at a high trophic level. On the other hand, a high-lipid diet allows for a very high biomagnification potential because of the high assimilation capacity of lipids, i.e., those contaminants are also absorbed very effectively. These two effects go a long way to explain why polar bears count among the organisms with the highest body burden of bioaccumulating compounds in the world, despite living in a remote environment far from the sources of these substances.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c00310>.

Detailed description of sample and silicone-coated vial preparation, equilibrium passive sampling, analytical methods, quality assurance, a list of analytes and samples, and chemical properties of selected compounds, tables of chemical concentration in samples and polymer, recovery rates,  $Z$  values,  $f$  and chemical activity values in diets and feces, relative contributions of lipids and NLOM to the bulk  $Z$  values,  $\text{BMF}_{\text{lim}}$  and fugacity-based BMF values, volume and  $Z$  values of the organs for a model polar bear and the mass and time for the bear to reach a steady state, and figures regarding the performance of equilibrium sampling, the daily uptake of PCBs, and the contributions of different dietary items to PCB exposure (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Frank Wania – Department of Chemistry and Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario, Canada M1C 1A4;  
orcid.org/0000-0003-3836-0901; Phone: +1-416-287-7225; Email: frank.wania@utoronto.ca

## Authors

Yuhao Chen – Department of Chemistry and Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario, Canada M1C 1A4;  
orcid.org/0000-0002-4196-4362

Ying Duan Lei – Department of Chemistry and Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario, Canada M1C 1A4

Jaap Wensvoort – Nutrition Science, Toronto Zoo, Toronto, Ontario, Canada M1B 5K7

Sarra Gourlie – Nutrition Science, Toronto Zoo, Toronto, Ontario, Canada M1B 5K7

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.est.2c00310>

## Notes

The authors declare no competing financial interest.

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