Response to Comment on "Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure"

The purpose of our paper (*1*) was to report concentrations of perfluoroalkyl contaminants (PFCs) in different components of an Arctic marine food web and to determine whether PFCs biomagnify in the food web. We also attempted to relate observed trophic magnification factors (TMFs) of PFCs to the octanol−water (K_{OW}), octanol−air (K_{OA}), protein−water (K_{PW}), and protein−air partition (K_{PA}) coefficients of PFCs with the goal to advance property activity relationships for bioaccumulation. Rayne and Forest have decided to comment on our assessment and utilization of the proper physical−chemical properties of these compounds in assessing their bioaccumulation behavior. While we welcome any and all discussion regarding our analyses, we feel the issues raised are, for the most part, divergent perspectives that have no bearing on the hypothesis, data quality, or conclusions of our study.

The physical−chemical properties of PFCs are not well-known as their measurements have proven to be challenging, and methods to compute these properties are uncertain because of a lack of reliable empirical data that can be used as training or validation data sets in Quantitative Structure Activity Relationships. There are several computer programs (e.g., SPARC, EPI Suite, COSMOther, ClogP) that can estimate K_{OW} and K_{OA} values based on molecular structure (*2*). However, K_{OW}s and K_{OA}s calculated by these methods differ by orders of magnitude (*2*). Also, recent updates of SPARC produced large differences in K_{OW} and K_{OA} estimates compared to previous versions.

In our study, we used SPARC-calculated log K_{OW} values for PFOS, PFOSA, and C_6−C_{11} PFCAs, reported in Arp et al. (*2*). We adjusted log K_{OW} values, equal to one log unit less than SPARC estimates based on suggestions by Dr. David Ellis. As Arp et al. (*2*) did not investigate PFDoA and PFTA, log K_{OW} and log K_{OA} values of these longer chain PFCAs were estimated from linear regression of SPARC calculated values for C_6−C_{11} PFCAs (*2*) versus molecular weight.

The log K_{OW} value for PFTA in Table S3 of our paper (log K_{OW} = 9.0) is a typographical error and should be log K_{OW} = 9.8. Log K_{OA} values of PFOS and PFOSA in Table S3 (7.8 and 8.4) are the COSMOtherm calculated values, rather than SPARC values (6.2 and 4.3). This exemplifies the wide range in calculated partition coefficients of PFCs. If SPARC calculated log K_{OA} values are used instead of the higher COSMOtherm values, there is no significant change in the TMF-log K_{PA} regressions reported in our paper (*1*), i.e., TMF = $[-4.20 \cdot \log K_{PA}]^2 + [44.1 \cdot \log K_{PA}] - 111$ ($R^2 = 0.32$, $P > 0.05$) using SPARC estimates and TMF = $[-0.91 \cdot \log K_{PA}]^2 + [7.20 \cdot \log K_{PA}] - 9.32$ ($R^2 = 0.10$, $P > 0.05$) using COSMOtherm values.

Because of the high uncertainty in the estimation of K_{OW} and K_{OA}, it is premature to classify PFCs based on these properties. However, the bioaccumulation behavior of PFCs can be classified in terms of the behavior expected from K_{OW} and K_{OA}. For example, the relatively low observed bioconcentration factors of C_7−C_{11} PFCAs (log BCFs ∼0.6−3.4) in fish indicates a bioaccumulation behavior in fish that resembles that of low K_{OW} chemicals (*3*). The observed biomagnification of PFOS and PFCAs in upper trophic level air-breathing wildlife (seabirds, seals, whales, polar bears) is consistent with a bioaccumulation behavior that involves slow aerial respiratory elimination, typical for chemicals with a high K_{OA}.

We agree with Rayne and Forest that it is important to recognize the potential ionization potential of PFOSA as PFOSA may be a mild acid. The calculated pK_a of PFOSA is 6.24 and SPARC estimates a distribution coefficient (log D) of ionized + un-ionized forms in blood (pH = 7.4) equal to 4.7, which is somewhat lower than the SPARC calculated partition coefficient of the neutral form of PFOSA (i.e., log P = 5.8). However, it is equally important to consider the pH of the digestive tract as the diet is an important route of uptake in mammals and fish. The pH of the digestive tract varies from approximately 2 to 7.4, which means that if PFOSA is indeed a mild acid, it can be expected to be largely in a nonprotonated form at several stages during the uptake process. In many fish species, the pH at the gill lamellae is mildly acidic as carbon dioxide excretion reduces the pH below the pH of the ambient water (*4*). Thus, with regard to gill uptake in fish, it is not unreasonable to view PFOSA in its unprotonated form.

It is also important to note that detailed analyses (empirical or theoretical) regarding pH and acidity of PFOSA have yet to be published. Conversely, PFOSA has been commonly characterized as a "neutral perfluoralkyl sulfonamide (PFAS)" which includes *N*-ethylperfluorooctane sulfonamide (Et-FOSA), *N*-methyl perfluorooctane sulfonamidoethanol (Me-FOSE), *N*-ethyl perfluorooctane sulfonamidoethanol (Et-FOSE), and *N*-methyl perfluorooctane sulfonamidethylacrylate (Me-FOSEA). These compounds are often referred to as "neutral PFOS precursors" in the literature. For example, analytical methodologies for PFC residue analysis often involves separation of the neutral PFAS fraction (including PFOSA), which can be analyzed by GC/MS, rather than LC/MS (*5, 6*).

Also, we question Rayne and Forest's comparison of PFOSA with various sulfonamide antibacterial pharmaceuticals. Specifically, one must use caution when comparing the behavior of relatively small, water-soluble compounds such as sulfapyridine ($C_{11}H_{11}N_3O_2S$; 249 g·mol^{-1}, pK_a = 8.4), sulfisomidine ($C_{12}H_{14}N_4O_2S$; 278 g·mol^{-1}; pK_a = 7.4), and sulfadimethoxine ($C_{12}H_{14}N_4O_4S$; 310 g·mol^{-1}, pK_a = 5.9), to relatively large molecules like PFOSA ($C_8F_{17}SO_2NH_2$; 499 g·mol^{-1}, pK_a = 6.24). Unlike the sulfonamide antibacterial drugs, PFOSA exhibits a fully fluorinated 8-carbon chain backbone, which may ultimately counteract any ionization of the amide group. Further empirical validation is needed to better understand the partitioning behavior of PFOSA under environmentally and toxicologically relevant pH.

We agree that increasing hydrophobicity due to increasing perfluoroalkyl chain length is a key factor affecting biological partitioning behavior of perfluorinated acids. In our paper we state that thermodynamics and equilibrium partitioning remain key determinants in the bioaccumulation potential of these compounds (*1*). However, there is currently a lack of empirically derived distribution coefficients (log D) for PFCs. Hence, a detailed discussion on the role of the physical chemical properties of PFCs is somewhat premature at this point. However, we are optimistic that future experiments focused on assessing protein−water equilibrium distributions (i.e., K_{PW}) and protein normalized BCFs and BAFs will garner a better understanding of the equilibrium partitioning of PFCs in aquatic systems. Ultimately, this will aid development of mechanistic models with the capability to predict envi-

10.1021/es901812c CCC: $40.75
Published on Web 07/09/2009

ronmental fate and bioaccumulation of these emerging contaminants of concern in the environment.

Literature Cited

(1) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Surridge, B.; Hoover, D.; Grace, R.; Gobas, F. A. P. C. Perfluoroalkyl contaminants in an Arctic marine food web: Trophic magnification and wildlife exposure. *Environ. Sci. Technol.* **2009**, *43*, 4037–4043.

(2) Arp, H. P.; Niederer, C.; Goss, K. U. Predicting the partitioning behavior of various highly fluorinated compounds. *Environ. Sci. Technol.* **2006**, *40*, 7298–7304.

(3) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2003**, *22*, 196–204.

(4) Randall, D. J.; Tsui, T. K. Tribute to R. G. Boutilier: acid-base transfer across fish gills. *J. Exp. Biol.* **2006**, *209*, 1179–1184.

(5) Tomy, G. T.; Budakowski, W.; Halldorson, T.; Helm, P. A.; Stern, G. A.; Friesen, K.; Pepper, K.; Tittlemier, S. A.; Fisk, A. T. Fluorinated organic compounds in an eastern Arctic marine food web. *Environ. Sci. Technol.* **2004**, *38*, 6475–6481.

(6) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr., A* **2005**, *1093*, 89–97.

Barry C. Kelly, Michael G. Ikonomou, Joel D. Blair, Blair Surridge, Dale Hoover, Richard Grace, and Frank A. P. C. Gobas

School of Resource and Environmental Management, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, Institute of Ocean Sciences, Fisheries and Oceans Canada, 9860 West Saanich Road, Sidney, British Columbia, Canada, V8L 4B2, and AXYS Analytical Services Ltd, 2045 Mills Road, Sidney BC Canada, V8L 5X2

ES901812C