

Comment on "Detection of Perfluorooctane Surfactants in Great Lakes Water" and "Mass Budget of Perfluorooctane Surfactants in Lake Ontario"

We read with interest and concern the recent papers by Boulanger et al. in which they report on the measurement of perfluorooctane surfactants in Great Lakes water (1) and air (2) and calculate a mass budget for these compounds in Lake Ontario (2). In addition, these authors claim to report the first detection of PFOSulfinate in lake water (1) and PFOS in air (2). We have a number of concerns with respect to data quality in these papers. The community of academic, industrial, and governmental researchers that work with fluorochemicals unanimously agree that it is imperative that the data published on fluorochemicals be of the highest quality because these data serve as a basis for making regulatory decisions (3). Our reasons for concern are outlined below:

Analytical Method Validation and Characterization. The authors report the development and use of a solid-phase extraction method for the measurement of several fluorinated compounds in lake water (1). However, as written, the description of the methodology is confusing; hence, reproducing it would be difficult. For example, the number of C18 cartridges used, the solvent in which the standards were applied to the cartridges, and exactly how they are eluted should be clarified. Moreover, the spike and recovery experiments were conducted by spiking "... to achieve a concentration in the extracted water of 10 ng/mL". However, 10 ng/mL is 10 000 ng/L, and this concentration is 2 orders of magnitude higher than the highest concentration reported (PFOS at 121 ng/L; Table 4).

In the same paper, the authors also report that the SPE method recovered $0.6 \pm 1\%$ of the PFOSulfinate standard (Table 3) (1). Despite the low recovery of the PFOSulfinate standard, the authors report concentrations for PFOSulfinate (Table 4). The authors hypothesize that poor PFOSulfinate recoveries are due to transformation to PFOS as evidenced by high PFOS recoveries of $176 \pm 8\%$. If this transformation reaction is fast (e.g., on the time scale of a laboratory spike and recovery experiment), then this raises the question of whether one would expect PFOSulfinate to occur and therefore be measurable in lake water.

In addition, there is a dearth of information regarding the analytical method used in Boulanger et al. (2) to measure these compounds in air samples collected above Lake Erie and Lake Ontario. For example, the limit of quantitation and limit of detection for the analytical method are not reported for the reader to evaluate. This is a potential concern given the relatively small volumes of air sampled ($95\text{--}378\text{ m}^3$). In addition, the authors discuss the use of XAD-2 resin, in series, to trap gas-phase compounds; however, the authors do not provide information on analyte breakthrough during sampling.

Use of Appropriate Field Blanks. The ubiquitous presence of these chemicals in the field and laboratory is widely recognized (3). The use of appropriate field blanks is critical for unambiguously determining concentrations of these compounds in the environment (3). The field blanks in these studies appear to consist of the air sampling media (XAD-2 resin) (2) or lake water solid-phase extraction cartridge (C18

SPE cartridge) (1) being transported, sealed, to and from the field (a trip blank) with no exposure to the sampling apparatus or ship environment. For the measurement of perfluorooctane surfactants in lake water, true field blanks should have included the tubing, stainless steel tanks, and pentaplate filters with glass fiber inserts (1). We have found that filters can retain fluorochemicals, including PFOS, from water samples, thereby causing negative artifacts. In addition, some filters are contaminated with fluorochemicals and result in positive artifacts. In addition, ships are well-recognized sources of pollutants (4), and this may be also true for fluorochemicals, which may be used onboard the ship. Without conducting a true field blank that accounts for media exposure to all potential sources of contamination, it is not clear what the actual field blank concentrations are for these chemicals.

Use of Mass Spectrometry. We are concerned that Boulanger et al. (1, 2) only discuss the use of a single quadrupole HPLC/MSD system to quantify fluorochemicals in lake water and air and that LC/MS/MS was not used to confirm the identity of all the compounds. In Boulanger et al. (1), the authors state that they used ion trap LC MS/MS to confirm analyte identities in 10% of the samples. However, this was done by direct infusion of the samples into the mass spectrometer without chromatographic separation. Direct infusion of a complex mixture containing structurally related analytes and co-extracted matrix interferences may not necessarily provide unequivocal confirmation of analyte identity (3). In our experience, good LC separation with one or more diagnostic transitions are needed even with MS/MS for unequivocal identification of fluorochemicals. Moreover, the authors did not explain why the triple quadrupole LC/MS/MS system (the standard technique for measuring these compounds in the environment) (3) was used only to confirm the identity PFOS but none of the other analytes. Given that this is the first report of the PFOSulfinate, triple quadrupole LC/MS/MS should have been used to unequivocally confirm the presence of PFOSulfinate in the lake water samples.

Detection of PFOS in Air. The authors state that they have detected PFOS in air samples for the first time (2). However, PFOS has been previously reported in air (5). In addition, the authors report PFOS concentrations in four of the eight air samples collected by ship on Lake Erie and Lake Ontario above an unreported method detection or quantitation limit (Table 2). We are concerned that these measurements may be artifacts that are unaccounted for because of the use of inappropriate field blanks and/or the use of only LC/MS and not LC/MS/MS to unequivocally confirm the identity of PFOS in these air samples.

Wastewater Treatment Discharge Estimation. Although it is likely that domestic wastewater treatment plants are a source of these compounds to the Great Lakes, we are concerned that the authors may have significantly overestimated this source by using the wastewater effluent concentrations reported by 3M (2). First, it is important to know if the 3M wastewater data used for the mass balance study were for wastewater samples obtained before or after the phase out of the 3M C8-based chemistry in 2002 because the mass balance study was conducted in 2003. The authors should also indicate if the 3M wastewater data were based on samples collected from municipal wastewater treatment plants or industrial wastewater treatment plants.

In conclusion, we are concerned that the research described in these manuscripts (1, 2) is lacking given the potential for contamination and the need for unequivocal identification of these compounds when attempting to measure them in complex environmental matrixes. This is especially important given that the authors claim to have detected PFOSulfinate in lake water and PFOS in air for the first time.

Literature Cited

- (1) Boulanger, B.; Vargo, J.; Schnoor, J. L.; Hornbuckle, K. C. Detection of perfluorooctane surfactants in Great Lakes water. *Environ. Sci. Technol.* **2004**, *38*, 4064–4070.
- (2) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. Mass budget of perfluorooctane surfactants in Lake Ontario. *Environ. Sci. Technol.* **2005**, *39*, 74–79.
- (3) Martin, J.; Kannan, K.; Berger, U.; de Voogt, P.; Field, J.; Franklin, J.; Giesy, J.; Harner, T.; Muir, D.; Scott, B.; Kaiser, M.; Jarnberg, U.; Jones, K.; Mabury, S.; Schroeder, H.; Simcik, M.; Sottani, C.; van Bavel, B.; Karrman, A.; Lindstrom, G.; van Leeuwen, S. Analytical challenges hamper perfluoroalkyl research. *Environ. Sci. Technol.* **2004**, *38*, 249A–255A.
- (4) Lohmann, R.; Jaward, F.; Durham, L.; Barber, J.; Ockenden, W.; Jones, K.; Bruhn, R.; Lakaschus, S.; DAchs, J.; Booij, A. Potential contamination of shipboard air samples by diffusive emissions of PCBs and other organic pollutants: implications and solutions. *Environ. Sci. Technol.* **2004**, *38*, 3965–3970.

- (5) Sasaki, K.; Harada, K.; Saito, N.; Tsutsui, T.; Nakanishi, S.; Tsuzuki, H.; Koizumi, A. Impact of airborne perfluorooctane sulfonate on the human body burden and the ecological system. *Bull. Environ. Contam. Toxicol.* **2003**, *71*, 408–413.

Jennifer A. Field*

Department of Environmental and Molecular Toxicology
Oregon State University
Corvallis, Oregon 97331

Staci Simonich

Department of Environmental and Molecular Toxicology
and Department of Chemistry
Oregon State University
Corvallis, Oregon 97331

Douglas Barofsky

Department of Chemistry
Oregon State University
Corvallis, Oregon 97331
ES050214M