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Response to Comment on “Detection of Perfluorooctane Surfactants in Great Lakes Water” and “Mass Budget of Perfluorooctane Surfactants in Lake Ontario”

We thank the writers for calling attention to our recent efforts to understand the fate of perfluorooctane compounds in the Great Lakes. We agree that data published on fluorochemicals must be of the highest quality. The writers' concerns, however, are unfounded. Our research methods used state-of-the-art instrumentation, tested methods, appropriate care to prevent background contamination, and quantitative evaluation of the uncertainties in all our numbers. We stand by our findings.

Analytical Methods. Some details were omitted in the original paper in the interest of printed space (1), and we appreciate the opportunity to provide those details here. During field sampling and laboratory retention experiments, a single 10 g Alltech C18 Extract-Clean High Capacity Solid-Phase Extraction (SPE) cartridge was used to process 50 L of water. A large sample volume was selected for this sampling cruise because we expected that the lake water concentration of perfluorinated organic compounds would be very low.

To test the retention of the C18 cartridge for the analyzed perfluorinated compounds, we performed a laboratory experiment using tap water and a known mass of our target compounds. We spiked 20 μ L of concentrated standard solution containing ~200 ng of each analyte (in methanol) onto the top of the cartridge. Fifty liters of tap water was then pushed through the spiked cartridge. After the 50 L of water was processed, the cartridge was eluted with 20 mL of methanol. The resulting methanol *extract* concentration (10 ng/mL) is within the calibrated range used to measure our field sample extracts. For sample processing, the C18 SPE cartridges were eluted with four 5 mL aliquots of methanol using a vacuum extraction chamber. (The manuscript incorrectly stated five 4 mL aliquots). More specifically, the processed cartridges were attached to a disposable flow control valve liner and inserted into the vacuum extraction chamber. Five milliliters of methanol eluent was placed atop the saturated C18 resin within the cartridge. The vacuum pump (GAST Vacuum Pump, MFG Corp.) was turned on, and the cartridge was eluted. The eluent was collected in a 30 mL polycarbonate bottle. After the pump was turned off and the pressure slowly released from the chamber, the 30 mL polycarbonate bottle was taken out of the chamber. The process was repeated three additional times. From each 5.0 mL of eluent, 300 μ L was placed into an autosampler vial, capped, and analyzed.

The results of these retention experiments confirmed that the C18 cartridge adequately retained our compounds of interest, with the exception of PFOSulfinate. We decided to report concentrations for PFOSulfinate in Great Lakes water, without correction, because we found evidence of a decay reaction occurring on the cartridge processed with tap water. On the cartridges spiked with our target compounds and eluted with 50 L of tap water, we recovered almost no PFOSulfinate and 76% more PFOS than what was injected. We hypothesized in our manuscript that PFOSulfinate undergoes a hydrolysis-like reaction in the C18 cartridge eluted with tap water, adding oxygen, to become PFOS. We further stated that the exact mechanism of the reaction is not known but may be due to the presence of minerals in the tap water that may (or may not) be present in lake water.

We are confident in our determination of PFOSulfinate based on HPLC retention time, quantification ion, and confirmation by ion trap mass spectrometry. Although the behavior of this compound in the two tested water matrixes were not the same, we think these results are interesting and should be reported.

Our field blanks showed very low masses of the target compounds and are reflective of the background contamination contributed by our sample handling. The field blanks in our studies were taken out of the sealed containers while in the field but were not actively processed by pulling air or water through the resins. For the water field blanks, the C18 cartridges were put on the lab benchtop and left out during one of the sampling sessions. For the air field blanks, the XAD and filters were installed in the air sampler, but the vacuum pump was not turned on. We were certainly concerned about the potential for contamination from the sampling systems, especially for the water samples. However, there is no foolproof way to test it directly. We think that the potential for contamination is low because the tanks, pipes, and filter system have only been used for Great Lakes water sampling and have been used constantly during the sampling season. We think it is reasonable to assume that the sampling system is at steady state with respect to uptake and loss of fluorinated compounds to the sampling system. The glass fiber filter itself was combusted prior to use; therefore, there is no reason to believe that this would serve as a source of contamination. On the other hand, the filter could have retained some of the compounds, and our reported concentrations may underestimate actual concentrations. Because we did not extract the filter, we cannot address this concern directly. In the case of the air samples, we used a yardarm sampler that extends the air samplers about 3 m off the bow of the ship. We have previously shown that this sampling modification reduced ship effects for organic compounds in air (2). Both the air sampling and water sampling protocols are well-recognized research methods for trace level detection of persistent organic compounds in natural systems.

We are aware that other researchers have recommended use of a liquid chromatograph with triple quadrupole mass spectrometry (LC/MS/MS) due to reported problems from interferences and artifacts that arise during analysis of the compounds in fish or organic matter (3). However, Great Lakes water and air have very low organic content and are much less complex than biological matrixes. We also now know that with sufficient sample preparation (such as SPE utilized in our research), LC/MS can and has been employed to measure and quantify perfluorinated compounds in various environmental matrixes including air (4, 5), water (1), and even human blood (6); not only by our group, but by at least two others as well. [We now recognize a paper by Sasaki et al. (4) as the first to report on the presence of PFOS in air samples and apologize for not seeing the paper at an earlier time.]

We used ion trap LC/MSⁿ to confirm analyte identity in 10% of the water samples we examined and triple quad LC/MS/MS to confirm PFOS in our water sample extracts. We found no evidence of matrix effects in any of our samples. Because of PFOS's verification using three different techniques in our own study, we have no reason to believe that the LC/MS quantification combined with the LC/MSⁿ verifications were not adequate to identify and report on the seven other compounds.

Mass Budget for Perfluorinated Compounds in Lake Ontario. The mass budget exercise reported in our recent

paper (5) provided two important outcomes. First, the mass budget illustrates that wastewater discharge is the major source of PFOS to the lake. Second, the steady-state analysis shows that the measured concentrations are reasonable and consistent, given the previously published estimates of perfluorinated compounds in wastewater effluent (7). Since the wastewater sources of perfluorinated compounds are not known for any wastewater effluents in the Lake Ontario watershed, we had to utilize available data for North American wastewater effluent concentrations regardless of the year or location of sampling. The source of the wastewater treatment concentrations used in the budget was well-discussed and cited in both the introduction and discussion of the paper. When utilized, the values are reported as mean concentrations with associated standard deviations. Caveats associated with using the 3M values are also discussed. Nevertheless, additional research and monitoring studies are needed to reduce the uncertainty in these annual loadings to Lake Ontario and other natural waters. Furthermore, additional research and monitoring studies are needed to identify plants with unusually high concentrations of these compounds in their effluents. Without action, these compounds are likely to be continually introduced to wastewater treatment plants, because of their ubiquitous usage in consumer products for over 50 years.

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