

2009, Volume 43, Pages 1134–1140

James M. Armitage, Matthew MacLeod, and Ian T. Cousins:
Modeling the Global Fate and Transport of Perfluorooctanoic
acid (PFOA) and Perfluorooctanoate (PFO) Emitted from Direct
Sources Using a Multispecies Mass Balance Model

In Armitage et al. (1), we reported the results of a global-scale modeling study investigating the fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) using a multispecies mass balance model. For these simulations, marine aerosol generation was not included as a surface-to-air exchange process for PFO(A). However, we attempted to characterize the potential importance of this process using the following approach (see Supporting Information of ref 1 for complete details). As a first approximation, the gross flux of PFO(A) ($F_{\text{PFO(A)}}$) on marine aerosols ($\text{kg m}^{-2} \text{yr}^{-1}$) ejected from the ocean surface can be calculated using eq 1.

$$F_{\text{PFO(A)}} = [\text{PFO(A)}](EF)(F_0)(3.65 \times 10^{-19}) \quad (1)$$

where $[\text{PFO(A)}]$ is the ocean water concentration of PFO(A) (pg L^{-1}), EF is the enrichment factor for PFO(A) in the surface microlayer/marine aerosols, F_0 is the marine aerosol production flux ($\text{mg m}^{-2} \text{d}^{-1}$), and the factor 3.65×10^{-19} is used to convert $F_{\text{PFO(A)}}$ into the correct units. This flux can be used to estimate the transfer of PFO(A) from the ocean to the atmosphere (kg yr^{-1}) by multiplying by the surface area of ocean being considered. Using a F_0 based on Grini et al. (2), we estimated the gross flux of PFO(A) in the northern hemisphere to be in range of approximately $<1.5\text{--}35 \text{ kg yr}^{-1}$ for the year 2005 and concluded that this process was unlikely to be important on a hemispheric scale. However, through discussions with Prof. David Ellis of the Canadian Centre for Environmental Modeling and Chemistry (CEMC), we realize that this estimated flux is biased low because the assumed value of F_0 represents the dry mass of salt rather than the mass of associated seawater. A second issue worth considering is that the size range of aerosols included in this F_0 is not representative of the complete range of aerosols ejected across the air–sea interface.

With respect to the first issue, a factor of ~ 30 is required to adjust the F_0 to represent the appropriate mass flux (see, e.g., ref 3). Correcting this error yields a gross flux in the range of $<45\text{--}1000 \text{ kg yr}^{-1}$ if all other assumptions are kept the same. This revised value is still small in comparison to the estimated global emissions to air for the same year (20–45 t).

With respect to the second issue, the F_0 from ref 2 includes accumulation mode and coarse aerosols up to a radius of $25 \mu\text{m}$ (sea salt aerosols up to approximately $20 \mu\text{m}$ are found in the atmosphere). However, as discussed in refs 4 and 5, sea spray droplets with a radius up to $500 \mu\text{m}$ or larger can be generated at the air–sea interface, particularly once wind speeds (at 10 m height) are in excess of $\sim 7\text{--}11 \text{ m s}^{-1}$ (4). Based on the sea spray generation function presented in ref 4 and assuming annual average wind speeds over oceans of $5\text{--}10 \text{ m s}^{-1}$, we estimate that the volume of water ejected across the air–sea interface per m^2 including these larger droplets is approximately 2–3 orders of magnitude higher than the new value used above (including the correction for dry salt to seawater mass). These larger aerosol droplets are suspended above the air–sea interface for only a limited period of time, i.e., $<1\text{--}10 \text{ s}$ (6) and hence have no long-range transport (LRT) potential. However, if the hypothesis forwarded by McMurdo et al. (7) regarding aerosol production and the mediation of water–air transport of gaseous PFOA is representative of actual field conditions (i.e., rapid

transfer of PFOA from aerosols of all sizes to the atmosphere with a half-life ($t_{1/2}$) of 7.2 s), at least some fraction of the mass of PFO(A) associated with larger droplets will be transferred into the gas phase. Given the uncertainties associated with the sea spray generation function and the lack of data characterizing the behavior of PFO(A) associated with marine aerosols under actual field conditions, we do not provide any additional calculations here. However, we believe that the statement in Armitage et al. (1) that marine aerosol generation is unimportant as a source of PFO(A) to the atmosphere on a hemispheric scale should be disregarded for the time being. Additional research on this process is clearly required before any definitive statements can be made. Representative field measurements, although costly and difficult to obtain, would be particularly valuable.

The error, and the large uncertainty in the estimated PFO(A) flux associated with marine aerosol generation, are of minor importance to the overall conclusions presented in Armitage et al. (1). Including marine aerosol generation in model calculations would have the most influence on global-scale simulations assuming $pK_a = 0$ and no emissions to air (i.e., localized deposition). Under these assumptions, atmospheric LRT is negligible, and water–air transport of PFO(A) related to marine aerosol generation could therefore result in substantial differences in model output, at least in relative terms. However, it should be recognized that the model results published in ref 1 are conservative in the sense that marine aerosol generation can only increase the LRT potential of PFO(A) emitted from direct sources. Therefore, the conclusion that emissions from direct sources have some potential to impact remote terrestrial environments remains valid. The conclusion that oceanic transport of PFO(A) to remote regions is a key pathway controlling the fate of this compound and the exposure of remote marine environments also remains valid.

Literature Cited

- (1) Armitage, J. M.; MacLeod, M.; Cousins, I. T. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. *Environ. Sci. Technol.* **2009**, *43*, 1134–1140.
- (2) Grini, A.; Myhre, G.; Sundet, J. K.; Isaksen, I. S. A. Modeling the annual cycle of sea salt in the global 3D model Oslo CTM2: Concentrations, fluxes and radiative impact. *J. Climate* **2002**, *15*, 1717–1730.
- (3) Spillane, M. C.; Monahan, E. C.; Bowyer, P. A.; Doyle, D. M.; Staben, P. J. Whitecaps and global fluxes. In *Oceanic Whitecaps and Their Role in Air-Sea Exchange Processes*; Monahan, E. C., Mac Niocaill, G., Eds.; D. Reidel Publishing Co., 1986.
- (4) Andreas, E. L. A new sea spray generation function for wind speeds up to 32 m s^{-1} . *J. Phys. Oceanogr.* **1998**, *28*, 2175–2184.
- (5) Andreas, E. L.; Edson, J. B.; Monahan, E. C.; Rouault, M. P.; Smith, S. D. The spray contribution to net evaporation from the sea: A review of recent progress. *Boundary-Layer Meteorol.* **1995**, *72*, 3–52.
- (6) Andreas, E. L. Time constants for the evolution of sea spray droplets. *Tellus* **1990**, *42B*, 481–497.
- (7) McMurdo, C. J.; Ellis, D. A.; Webster, E.; Butler, J.; Christensen, R. D.; Reid, L. K. Aerosol enrichment of the surfactant PFO and mediation of the water–air transport of gaseous PFOA. *Environ. Sci. Technol.* **2008**, *42*, 3969–3974.

ES901832B

10.1021/es901832b

Published on Web 07/08/2009