EVALUATION OF SOURCES OF PERFLUORINATED COMPOUNDS IN UPPER MISSISSIPPI RIVER WATER USING POLYTOPIC VECTOR ANALYSIS

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Introduction

In the last 10-15 years, perfluorinated compounds (PFCs) have been detected in surface water, groundwater, soil, air, biota, and human serum worldwide. PFCs are fluorinated alkyl compounds that have been used in the manufacture or are byproducts of polyfluorinated chemicals used in a variety of applications that include stain-resistant surface coatings for carpets, paper, upholstery, and textiles; firefighting foams; cosmetics; lubricants; and nonstick surface coatings for cookware.[1] While various investigators have characterized PFC concentrations in the environment, there is little information about the contribution of the different types of PFC sources to PFC concentrations in the environment.

Nakayama et al. recently published data for PFC concentrations in upper Mississippi River surface water that were collected from 88 sampling sites in the upper Mississippi River and Missouri River basins from March and August 2008 by various state and federal agencies.2 In this study, 177 surface water samples were collected and analyzed for perfluorobutanoic acid (C4), perfluoropentanoic acid (C5), perfluorohexanoic acid (C6), perfluoroheptanoic acid (C7), perfluorooctanoic acid (C8), perfluorononanoic acid (C9), perfluorodecanoic acid (C10), perfluoroundecanoic acid (C11), perfluorododecanoic acid (C12), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHS), perfluorooctananesulfonate (PFOS), and perfluorodecanesulfonate (PFDS). Because this data set has a large number of samples collected over a broad geographical area, and a fairly large number of PFCs (9) that were measured above the quantitation limit in at least 30% of the samples, it is a suitable data set for applying a statistical unmixing method, such as polytopic vector analysis (PVA), to identify the types of PFC sources that may be contributing to PFC concentrations in the upper Misssippi River and Missouri River basins and their contributions to the PFC levels in Mississipi River water.

Materials and Methods

For this analysis, PVA was applied to the surface water data presented by Nakayama et al. to evaluate the number of possible PFC sources contributing to PFC concentrations in the upper Mississippi River basin and their PFC chemical distributions. PVA was developed to analyze mixtures of chemicals in the environment by identifying the number of distinct chemical patterns, referred to as end members, that form a complex mixture, determining the chemical composition of each pattern, and determining the relative proportions of each pattern in each sample.[3]

To insure that the data set was sufficiently robust for the PVA analysis, the data set was reduced to contain only data for those PFCs that had detection frequencies greater than 30%. This reduced the number of PFCs considered from 13 to 9 with the exclusion on C10, C11, C12, and PFDS. In addition, only samples that had at least 3 PFCs detected were included. This decreased the number of samples included in the PVA from 177 to 129. To minimize any artificial results due to samples with PFC concentrations below the limit of quantification or detection, the contribution for a PFC in a sample that was less than the limit of quantification or detection was set equal to zero.

Standard methods for identifying the number of end members and determining their compositions and relative mixing proportions were used.[4]

Results and Discussion

The evaluation of this data set resulted in a PVA model with 5 end members that described 92.1% of the variance in the data set. Figure 1 presents the PFC composition for each of the five end members. End member

1 is characterized by contributions from C5, C6, C9, PFBS, and PFhS and is present in most samples at mixing proportions between 10% to 30% (Figure 2). The highest proportions of end member 1 are found in samples from the Illinois River near Peoria and downstream of Chicago (39-40.5%) and a sample from wastewater treatment plant (WWTP) effluent (40.4%). Given the consistent mixing proportion of this end member in the majority of samples and the higher mixing proportion in a sample from WWTP effluent, this end member most likely represents the contribution of PFCs due to WWTP discharge to the Upper Mississippi River water shed.

End member 2 is predominantly C4 and ranges from 10% to 50% is most samples upstream of where the Wapsipinicon River discharges to the Mississippi River. Downstream of that location the mixing proportion of this end member peaks at 93.9% and then declines to around 70% at the most downstream sample. Samples with profiles similar to this have been found in landfill leachate from Germany[5] and from groundwater near a landfill known to be impacted by fluorochemical manufacturing wastes.[6]

End member 3 is characterized by contributions of C6 and C7. The highest proportions (81.9%) of this end member are found in samples collected in the Upper Mississippi River upstream of Brainerd and Minneapolis-St. Paul, MN (Figure 2). Along the Mississippi River, the mixing proportion of this end member declines down to between 0 to 20% for samples downstream of Minneapolis-St. Paul, MN.

End member 4 is characterized by a high contribution from PFOS and lesser contributions from PFBS and PFHS and no contributions from the C4 through C9. The samples with the highest proportions of this end member (Figure 2) were collected from the Mississippi River near Brainerd, MN (85.2-87.3%), from the Missouri River near Kansas City, MO (73%), and from a creek that discharges to Wild Rice Lake Reservoir that may receive runoff from a fire training site at the Duluth International Airport (55-65%). This end member may be associated with historical use of fire fighting foam containing PFCs.

End member 5 is predominantly C8 with some contributions from PFOS, PFBS, and C9. The highest mixing proportions for this end member range from 40-49% and are from samples collected from the Mississippi River that are downstream of a fluorochemical facility in Cottage Grove, MN (Figure 2). For the majority of samples collected at other locations on the Mississippi River, this end member ranges from 10-30% in samples upstream of where end member 2 peaks.

Figure 1. PFC End Members Identified by PVA.

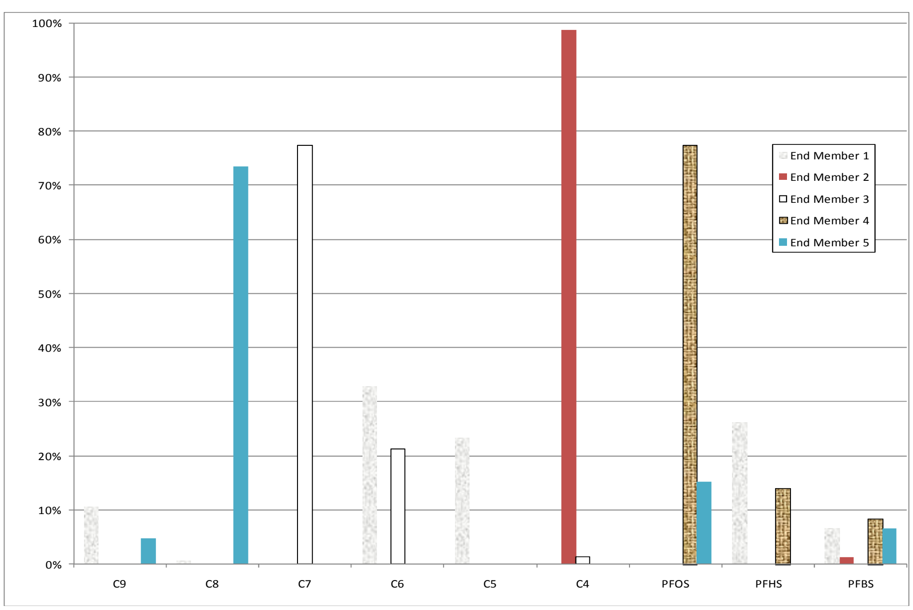
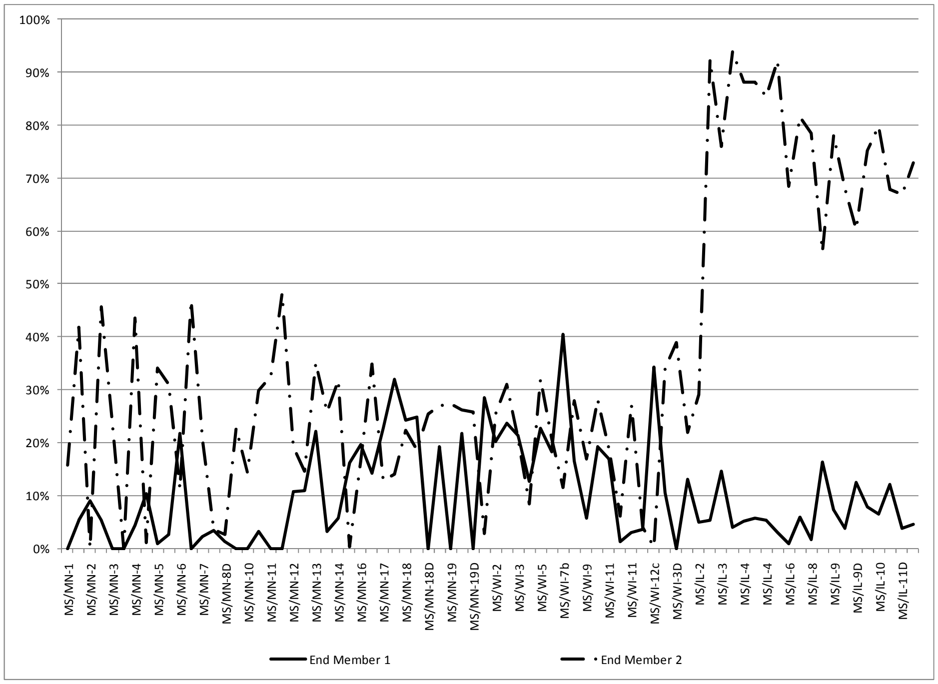
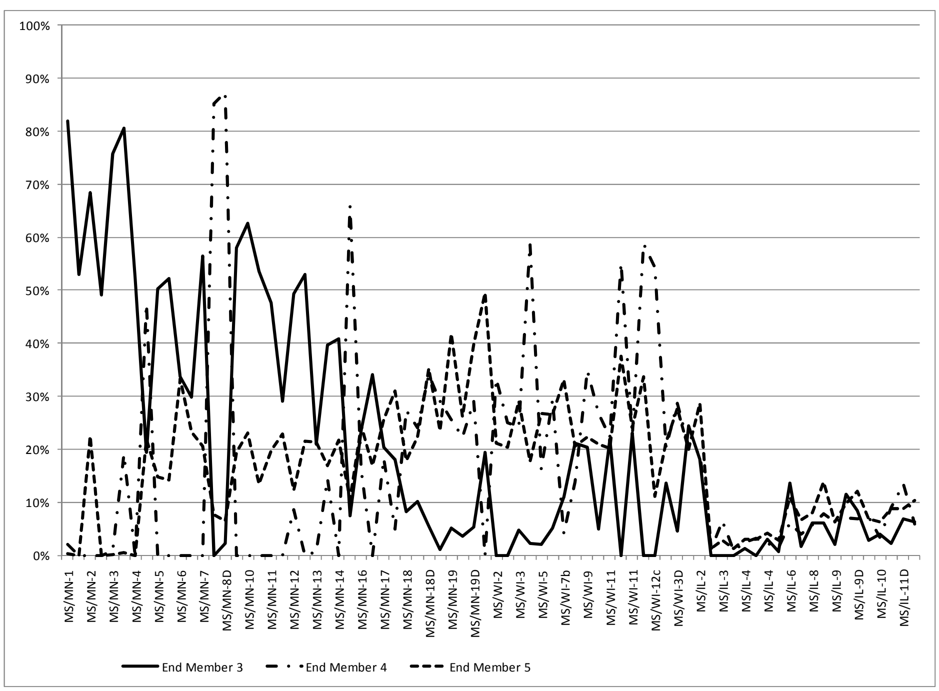


Figure 2. Mixing Proportions for PFC End Members for Samples Collected from the Mississippi River.





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