Perfluorinated compounds in the Ohio River Basin

Shoji F. Nakayama[1], Erich Emery[2], Marc A. Mills[3], John Spaeth[2]

1 National Research Council Associate at U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 West Martin Luther King Drive., Cincinnati, OH 45268, USA

2 Ohio River Valley Water Sanitation Commission, 5735 Kellogg Ave., Cincinnati, OH 45230, USA

3 U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 West Martin Luther King Drive., Cincinnati, OH 45268, USA

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Introduction

Contaminants of emerging concern (CECs) in waterways include pharmaceuticals and personal care products (PPCPs), akylphenols, endocrine disrupting chemicals (EDCs) and perfluorinated alkyl compounds (PFCs). Their distributions and persistence in the aquatic environment remain poorly defined and public awareness and concern about these materials is increasing. Among these compounds, the PFCs have been studied in a small number of U.S. watersheds, with data describing their longitudinal occurrence and concentration in large river systems still being very scarce. Because the Ohio River and its tributaries provide drinking water, irrigation, and recreation for 25 million people living in this basin, it is essential to determine the occurrence and concentration of the various PFCs in the surface water resources of this region. To meet this need, in the fall of 2009, the Ohio River Valley Water Sanitation Commission (ORSANCO) collaborated with U.S EPA to collect single grab samples from 22 locations on the Ohio River and some selected tributaries. The primary focus of this study was to document the occurrence and concentrations of CECs, including PFCs.

This study was designed to generate data as preliminary survey by the Commission and results would be used to guide future actions.

Site Description

In September and October, 2009, single grab samples were collected from 22 locations on the mainstem Ohio River and the lower reaches of tributaries.

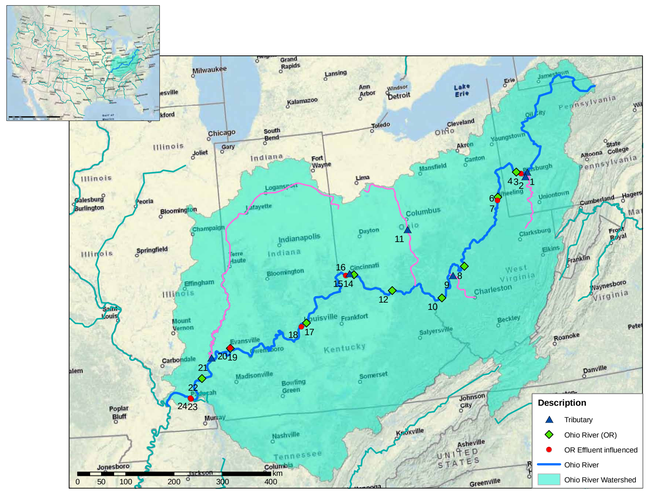

Figure 1. Sampling locations

Methods

Samples were collected using 2-L amber glass bottles (pre-cleaned with solvents, baked in a muffle furnace, and silanized) from a mid section of each river at each sampling site illustrated in Figure 1. Samples were immediately transferred to methanol rinsed high density polyethylene bottles, then stored on ice. Between sampling locations, collection equipment was rinsed with river water followed by ultrapure water for proper decontamination of the equipment. The bottles were shipped to Axys Anatytical Services (Sidney, BC, Canada). Since other target compounds were included in the same shipping event, a universal shipping procedure had to be used: samples were placed on ice and shipped by over night carrier. Ultrapure water was brought to the the field and poured into empty containers to serve as field blanks. Travel spike samples were also prepared by spiking two levels of PFCs into ultrapure water in the field at the time of collection.

Samples were extracted and analyzed by Axys Analytical using solid phase extraction and liquid chromatography–tandem mass spectrometry. Isotope dilution was employed for quantitation.

Results and Discussion

Travel spikes

Axys's protocol for sample preservation only required maintaining the samples on ice. According to our previous study, it is known that PFCs adsorb to the sample container wall during storage and a methanol rinse is required to recover the adsorbed PFCs. Since Axys's method did not involve the methanol rinse procedure, travel spikes were prepared to evaluate possible losses during sample transport and storage. It took 8–14 days from sample collection to extraction. Recovery for two levels of spikes in ultrapure water is shown in Table 1. Spiking into ultrapure water may or may not reflect actual situation for surface water samples, however, this result indicates that thorough evaluation of sample preservation, handling, and storage procedure is essential. Due to the lower recoveries for some target analytes, care should be taken when the resulting data is interpreted (it could be under estimated).

Table 1. Recovery of travel spikes at 20 and 200 ng/L in ultrapure water

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
Field spike 1 (ng/L)	15.2	13.5	13.7	14.2	11.6	12.2	10.1	7.96	3.1	13.0	9.67	4.19	NA
Recovery (%)	76.0	67.5	68.5	71.0	58.0	61.0	50.5	39.8	15.6	65.0	48.4	21.0	
Field spike 2 (ng/L)	215	196	199	211	174	178	181	113	43	177	149	79.1	NA
Recovery (%)	108	98.0	99.5	106	87.0	89.0	90.5	56.5	21.3	88.5	74.5	39.6	
MRL	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Results and Discussion (Cont.)

PFC concentrations

Results are shown in Table 2 and Figure 2. PFOS and carboxylates shorter than 8 were found in more than 90% of the samples. Concentrations were generally low (< 10 ng/L), however, some samples showed elevated concentrations. Possible point sources are speculated upstream of site 8 for PFOA and site 20 for PFHxS and PFOS. At site 20, the sample was collected within a wastewater plume. Generally samples from downstream of known wastewater discharges showed higher concentrations of both carboxylates and sulfonates than those from upstream sites. After site 8, elevated PFOA in the main stream of the Ohio River stayed relatively constant downstream.

Table 2. Descriptive statistics of PFC concentrations (MRL/2 = 0.5 was assigned to < MRL)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
%>MRL	90.9	95.5	90.9	90.9	100	36.4	22.7	4.55	4.55	31.8	13.6	90.9	4.55
Min	0.50	0.50	0.50	0.50	1.48	0.50	0.50	0.50	0.50	0.50	0.50	2.24	0.50
P25	1.38	1.39	1.75	1.33	3.54	0.50	0.50	0.50	0.50	0.50	0.50	2.81	0.50
Median	1.68	1.89	2.39	1.59	9.33	0.50	0.50	0.50	0.50	0.50	0.50	4.70	0.50
P75	2.63	3.24	3.70	2.50	14.4	1.18	0.50	0.50	0.50	2.46	0.50	6.69	0.50
P90	5.70	6.48	9.32	4.39	23.4	1.73	1.60	0.50	0.50	18.2	2.73	29.8	0.50
Max	15.7	13.7	14.7	9.14	35.2	8.08	8.04	3.02	4.75	111	8.91	669	1.60

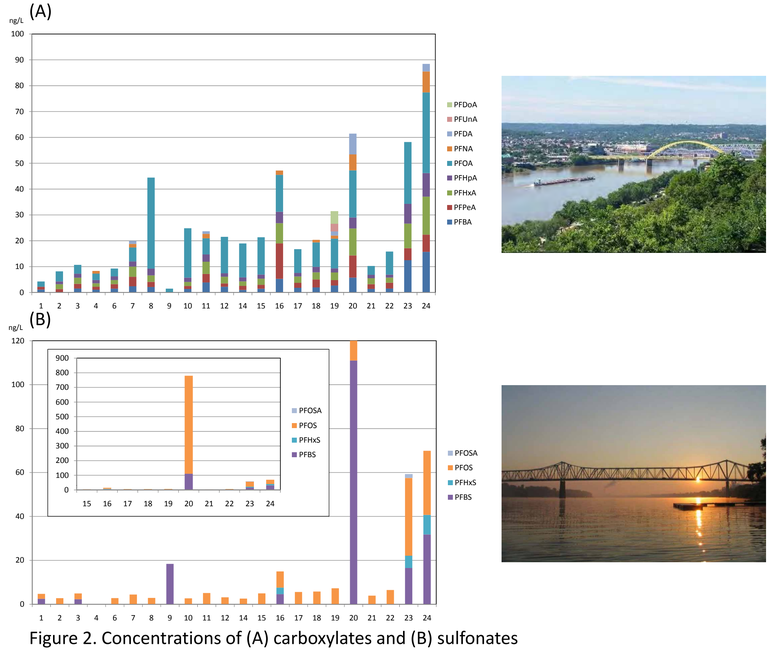

Figure 2. Concentrations of (A) carboxylates and (B) sulfonates