SUPPLEMENTARY INFORMATION

Biomonitoring of Perfluorochemicals in Plasma of New York State Personnel Responding to the World Trade Center Disaster

LIN TAO[†], KURUNTHACHALAM KANNAN[†,*], KENNETH M. ALDOUS[†], MATTHEW P. MAUER[‡], AND GEORGE A. EADON[†]

[†]*Wadsworth Center, New York State Department of Health and Department of Environmental Health Sciences, State University of New York at Albany, Empire State Plaza, PO Box 509, Albany, New York 12201-0509, USA*

[‡]*Bureau of Occupational Health, Center for Environmental Health, New York State Department of Health, 547 River Street, Troy, NY 12180, USA*

Chemical Analysis. PFOS, PFHxS, perfluorooctanesulfonamide (PFOSA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA) were analyzed in plasma samples using an ion-pairing extraction procedure and were determined by use of a high-performance liquid chromatograph (HPLC) with an electrospray tandem mass spectrometer (ES-MS/MS) (18,21,22). Approximately 0.5 mL of plasma, 1 mL of 0.5 M tetrabutyl ammonium hydrogen sulfate solution (adjusted to pH 10), and 2 mL of 0.25 M sodium carbonate buffer were added to a 15-mL polypropylene tube for extraction. After thorough mixing, 5 mL of methyl-tert-butyl ether (MTBE) was added, and the mixture was shaken for 20 min. The organic and aqueous layers were separated by centrifugation and an exact volume of MTBE (4 mL) was removed from the solution. The aqueous mixture was rinsed with MTBE and separated twice; all rinses were combined in a second polypropylene tube. The solvent was allowed to evaporate under nitrogen before being reconstituted in 0.5 or 1.0 mL of methanol. The sample was vortexed for 30 seconds and was passed through a 0.2-µm nylon filter into an autosampler vial; the final solvent volume was reduced to 0.2 mL prior to instrumental analysis.

Analyte separation was performed using an Agilent1100 series HPLC. Ten microliter of the extract was injected onto a 100 x 2.1 mm (5 µm; Thermo Electron Corporation, Bellefonte, PA) Betasil® C18 column with 2-mM ammonium acetate/methanol as the mobile phase starting at 10% methanol. At a flow rate of 300 µL/min, the gradient increased to 100% methanol at 10 min before reverting to original conditions at 12 min. For quantitative determination, the HPLC system was interfaced to

an API 2000 tandem mass spectrometer (Applied Biosystems, Foster City, CA) operated in the electrospray negative ionization mode. Instrumental parameters were optimized to transmit the $[M-K]^-$ ion before fragmentation to one or more product ions. Declustering potential and collision energies were optimized for each analyte and ranged from 35 to 90 V and 10 to 35 eV, respectively. Data were acquired by tandem mass spectrometry using multiple reaction monitoring at transitions, 499>99 for PFOS, 503>99 for $^{13}C_4$-PFOS, 497.7>77.7 for PFOSA, 398.7>79.7 for PFHxS, 298.7>79.7 for PFBS, 363>319 for PFHpA, 413>369 for PFOA, 417>372 for $^{13}C_4$-PFOA, 463>419 for PFNA, 513>469 for PFDA, and 563>519 for PFUnDA. When possible, multiple daughter ions were monitored for confirmation, but quantitation was based on a single product ion. In all cases, the capillary was held at -4 kV and the desolvation temperature was kept at 400°C.

Standards. Potassium salts of PFOS (86.4%), PFHxS (99.9%), and PFOA (98%) and PFOSA (95%) were provided by the 3M Company (St. Paul, MN). PFHpA, PFNA, PFDA, and PFUnDA were from Fluorochem Ltd (≥95% purity, Derbyshire, UK). Perfluorobutanesulfonate (PFBS; 99% purity, The 3M Company, St. Paul, MN),

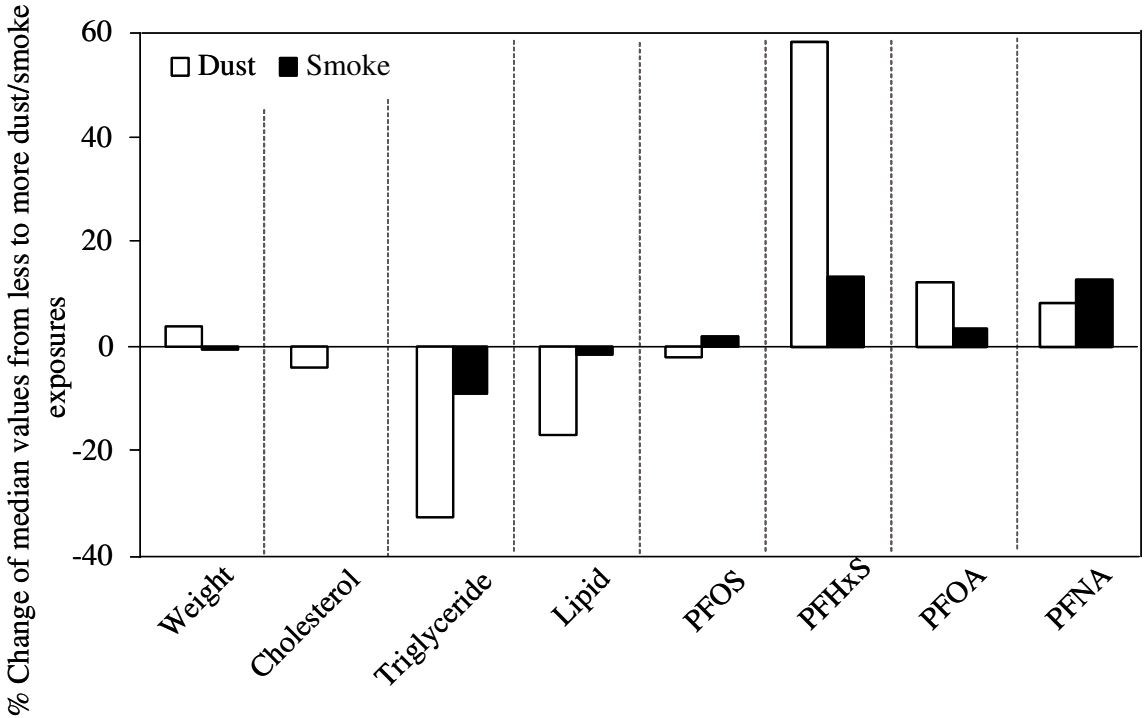

Figure S1. Percent change in (median values) body weight, cholesterol levels, triglyceride levels, lipid content, PFOS, PFHxS, PFOA and PFNA concentrations between less dust/smoke and more dust/smoke exposure groups.

Table S1. Spearman's correlation coefficient (r) and correlation matrix for perfluorochemical concentrations, age, body weight, cholesterol, triglyceride, and lipid content in New York State WTC responders exposed to dust and smoke (n=457).

	PFOS [a]	PFHxS	PFOA	PFNA	Age	Body Weight	Cholesterol	Triglyceride
PFHxS	0.442***							
PFOA	0.579***	0.531***						
PFNA	0.429***	0.304***	0.365***					
Age	0.039	-0.075	-0.094*	-0.095*				
Body Weight	0.039	0.044	0.057	0.056	0.202**			
Total cholesterol	-0.058	-0.068	-0.059	0.064	0.094*	0.108*		
Triglyceride	-0.065	-0.030	0.000	-0.127**	0.080	0.250**	0.291**	
Lipid%	-0.079	-0.126**	-0.078	-0.151**	0.106*	0.186**	0.559**	0.814**

[a] Level of significance denoted as $^{*}p \leq 0.05$, $^{**}p \leq 0.01$, $^{***}p \leq 0.001$.

Table S2. Spearman's correlation coefficient (r) and correlation matrix for perfluorochemical concentrations, age, body weight, cholesterol, triglyceride, and lipid content in each of the WTC exposure groups.

Symptomatic	PFOS [a]	PFHxS	PFOA	PFNA	Age	Weight	Cholesterol	Triglyceride
PFHxS	0.368**							
PFOA	0.411***	0.479***						
PFNA	0.353**	0.359**	0.412 ***					
Age	0.075	-0.102	-0.280*	-0.114				
Weight	0.055	-0.084	-0.013	0.053	0.276*			
Total Cholesterol	-0.086	-0.198	-0.210	0.109	0.199	0.199		
Triglyceride	-0.091	-0.092	-0.126	-0.126	0.152	0.242*	0.623***	
Lipid%	-0.101	-0.226	-0.267*	-0.219	0.203	0.078	0.675***	0.707***

Asymptomatic	PFOS [a]	PFHxS	PFOA	PFNA	Age	Weight	Cholesterol	Triglyceride
PFHxS	0.223							
PFOA	0.598***	0.217						
PFNA	0.281*	0.195	0.316**					
Age	-0.141	-0.236*	-0.201	-0.212				
Weight	-0.037	0.015	-0.097	-0.114	0.194			
Total Cholesterol	-0.074	-0.109	0.010	0.028	0.016	0.102		
Triglyceride	-0.144	-0.242*	-0.006	-0.395***	0.256*	0.126	0.138	

Lipid%	-0.009	-0.255*	-0.036	-0.157	0.249*	0.136	0.546***	0.674***

More dust	**PFOS** [a]	**PFHxS**	**PFOA**	**PFNA**	**Age**	**Weight**	**Cholesterol**	**Triglyceride**
PFHxS	0.438**							
PFOA	0.653***	0.484**						
PFNA	0.453**	0.468**	0.708***					
Age	0.070	0.088	0.047	0.014				
Weight	-0.084	-0.009	-0.226	-0.124	0.332			
Total Cholesterol	-0.151	-0.066	-0.202	-0.133	0.176	0.408*		
Triglyceride	-0.184	0.096	-0.045	0.016	0.084	0.035	0.147	
Lipid%	-0.227	-0.164	-0.258	-0.217	-0.055	0.080	0.618***	0.603***

Less dust	**PFOS** [a]	**PFHxS**	**PFOA**	**PFNA**	**Age**	**Weight**	**Cholesterol**	**Triglyceride**
PFHxS	0.313							
PFOA	0.555***	0.257						
PFNA	0.548***	0.387*	0.360*					
Age	0.416*	-0.055	0.266	0.208				
Weight	-0.098	0.121	-0.065	-0.276	0.032			
Total Cholesterol	-0.124	-0.102	-0.428*	-0.025	-0.119	-0.015		

Triglyceride	0.374*	0.203	0.082	0.032	-0.023	0.308	0.286	
Lipid%	0.235	-0.027	-0.191	0.013	-0.184	0.083	0.565**	0.818***

More smoke	**PFOS** [a]	**PFHxS**	**PFOA**	**PFNA**	**Age**	**Weight**	**Cholesterol**	**Triglyceride**
PFHxS	0.466***							
PFOA	0.618***	0.438***						
PFNA	0.488***	0.275***	0.352***					
Age	0.149	-0.008	-0.013	0.105				
Weight	0.096	-0.006	0.144	-0.040	0.212*			
Total Cholesterol	-0.034	-0.092	-0.125	-0.070	0.193*	0.102		
Triglyceride	-0.163	-0.090	-0.019	-0.164	0.110	0.312**	0.276***	
Lipid%	-0.158	-0.112	-0.060	-0.174*	0.187*	0.308**	0.582***	0.931***

Less smoke	**PFOS** [a]	**PFHxS**	**PFOA**	**PFNA**	**Age**	**Weight**	**Cholesterol**	**Triglyceride**
PFHxS	0.498***							
PFOA	0.561***	0.539***						
PFNA	0.365***	0.203*	0.184*					
Age	0.050	0.077	0.059	-0.174*				

Weight	0.083	0.115	0.079	-0.062	0.159			
Total Cholesterol	-0.087	0.011	0.148	-0.036	-0.007	0.033		
Triglyceride	0.019	0.061	0.068	0.092	-0.106	0.269**	0.196*	
Lipid%	0.009	0.024	0.087	0.064	-0.121	0.187 *	0.484***	0.931***

[a] Level of significance denoted as $^{*}p \leq 0.05$, $^{**}p \leq 0.01$, $^{***}p \leq 0.001$