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# Persistent organic pollutants in 9/11 world trade center rescue workers: Reduction following detoxification

James Dahlgren a,\*, Marie Cecchini b,1, Harpreet Takhar c,2, Olaf Paepke d,3

<sup>a</sup> UCLA School of Medicine, Occupational Medicine, 2811 Wilshire Blvd. Suite 510, Santa Monica, CA, USA
 <sup>b</sup> Foundation for Advancements in Science and Education, 4801 Wilshire Blvd. Suite 215 Los Angeles, 90010 CA, USA
 <sup>c</sup> James Dahlgren Medical, 2811 Wilshire Blvd. Suite 510, Santa Monica, CA, USA
 <sup>d</sup> ERGO Laboratory, 22305 Hamburg, Germany

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#### **Abstract**

Exposure to toxins following the September 11, 2001 attack on and collapse of the World Trade Center (WTC) is of particular concern given the ultra fine particulate dust cloud, high temperature combustion, and months-long fire. Firefighters, paramedics, police and sanitation crews are among the approximately 40 000 personnel who labored for weeks and months on rescue and cleanup efforts. Many of the rescue workers have subsequently developed symptoms that remain unresolved with time. This study characterizes body burdens of polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dioxins (PCDDs) in rescue workers and citizens exposed following the WTC collapse. Our research includes a pilot evaluation of a detoxification method aimed at reducing toxic burden. Many congeners were found at elevated levels, in ranges associated with occupational exposures. Post-detoxification testing revealed reductions in these congeners and despite the small study size, some reductions were statistically significant. Health symptoms completely resolved or were satisfactorily improved on completion of treatment. These results argue for a larger treatment study of this method and an overall treatment approach to address toxic burden.

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Keywords: Environment; Exposure; Dioxin; Dibenzofuran; PCB; Treatment

#### 1. Introduction

Rescue workers present at the World Trade Center (WTC) following the September 11, 2001 terrorist attacks were exposed to large quantities of dust, smoke and fumes from the building's collapse and subsequent fire. The fire at the WTC site burned for months. Firefighters, paramedics, police and sanitation crews were among the approximately

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40 000 personnel who labored for weeks and months in the immediate vicinity of the WTC. Personal Protective Equipment (PPE) use was inconsistent (Kipen and Gochfeld, 2002), and contaminant exposure occurred in a number of ways including dermal absorption and inhalation.

Many of the rescue workers developed persistent coughs, headaches, memory disturbances and other symptoms while working on the site. Two and a half years later, these symptoms persisted (Prezant et al., 2002). USEPA measured levels of benzene, dioxins and polychlorinated biphenyls (PCBs) in air and found these levels were elevated in the weeks after the collapse. (Litten et al., 2003) Dioxins slowly returned to normal background levels after three months. (Litten et al., 2003) The New York (NY) Department of Environmental Conservation (DEC) analyzed dust/ash samples collected nearby the WTC site.

<sup>\*</sup> Corresponding author. Tel.: +1 310 449 5525; fax: +1 310 449 5526. E-mail addresses: Dahlgren@envirotoxicology.com (J. Dahlgren), macecchini@comcast.net (M. Cecchini), htakhar@envirotoxicology.com (H. Takhar), olaf.paepke@web.de (O. Paepke).

<sup>&</sup>lt;sup>1</sup> Tel.: +1 323 937 991.

<sup>&</sup>lt;sup>2</sup> Tel.: +1 310 449 5525.

<sup>&</sup>lt;sup>3</sup> Tel.: +49 40 69 70 96 23.

The purpose of this study was two-fold: 1. To characterize body burdens of polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dioxins (PCDDs) in exposed rescue workers and citizen. 2. A pilot evaluation of a treatment method aimed at reducing toxic burden.

#### 2. Methods and materials

Seven men who were present at the WTC collapse and involved in the rescue and cleanup effort received treatment at the New York Rescue Workers Detoxification Project in April 2004 and agreed to participate in this study. Five were employed by the New York Fire Department (FDNY), one was a volunteer rescue worker and one worked at the nearby at the NY Stock Exchange. All were at the site the day of and several weeks after the collapse when exposure would have been the highest. The rescue workers used little or no protective respiratory gear during the WTC cleanup and all currently live or work in New York. The average age was 44 (range is 37–53).

These individuals volunteered to have their blood drawn to measure the levels of polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dioxins (PCDDs). Fifty milliliters of whole blood was drawn in chemically cleaned glass containers prepared by the analytic laboratory with anticoagulant with Teflon® tops containing no paper products. Blood was frozen and sent frozen on dry ice to Germany for polychlorinated dioxin and furan analysis at ERGO Laboratory, a World Health Organization certified dioxin laboratory. Analysis was performed by gas chromatography/high-resolution mass spectrometry by methods previously described (Päpke et al., 1989). Measured levels were converted to dioxin toxic equivalents (TEQ) using the 1998 WHO toxic equivalency factors (TEFs) (Van den Berg et al., 1998).

These subjects also participated in a series of testing including thorough medical examination, structured health and symptom questionnaires, and neurophysiological testing.

All tests, evaluations, and sample collections were repeated approximately one month after initial testing in order to provide a comparison. Following the second period baseline evaluation, the study subjects enrolled in the detoxification treatment regimen developed by Hubbard, which included exercise, sauna bathing and vitamin and mineral supplements developed to reduce the adverse effects of chemical exposures. (Schnare et al., 1982; Tretjak et al., 1990) On completion of treatment, all subjects had their blood drawn for post-treatment evaluation.

#### 3. Results

The measured dioxin, dibenzofuran, and PCB congener levels and TEQ for each subject before and after detoxification is presented in Table 1. Prior to detoxification treatment, five rescue workers (HB50605, WB5005, WB8008,

WB9009, WB13013) had elevated levels of 2,3,3',4,4'-PeCB (105), 2,3',4,4',5-PeCB (118) and/or 2,3,3',4,4',5-HxCB (156). Patient H 5-0605 was a firefighter who we initially tested in May 2003. Pre treatment, total mono-ortho PCB blood levels ranged from 19 ppb to 404 ppb (WHO-TEQ 8.2–133.3) with a geometric mean of 41 ppb (WHO-TEQ of 29.3). Pre-treatment, total non-ortho PCB blood levels ranged from 43 ppt to 328 ppt (WHO-TEQ 3.9–111.9), with a geometric mean of 81.8 ppt (WHO-TEQ of 13.1).

Table 2 displays the mean and median difference for each congener following detoxification. The *p*-value is calculated using the Wilcoxon singed-rank test, which is a non-parametric test that uses ranks of the data consisting of matched pairs. By using ranks, this test takes the magnitudes of the differences into account. Due to the small sample size, we cannot assume normality of the data. A non-parametric test is the best test for our study. The means and medians listed in Table 2 are for the differences between the congener before and after detoxification. Therefore, a positive score reflects a mean/median where the average levels of dioxin, dibenzofuran and PCBs dropped, while a negative score reflects where the average levels increased.

Following detoxification, calculated WHO-TEQs for mono-ortho PCB blood levels decreased by an average 65%, as shown in Fig. 1. Measured levels ranged from 15 ppb to 302 ppb (WHO-TEQ 3.6–133.3) with a geometric mean of 32 ppb (WHO-TEQ of 8). Non-ortho WHO-TEQs averaged a 57% decrease as shown in Fig. 2. Measured levels ranged from 33 ppt to 229 ppt (WHO-TEQ 1.6–17).

Mono-ortho and non-ortho PCB levels in rescue workers were measured twice in one month prior to detoxification to determine the change in levels, or the lack thereof, with the absence of treatment. As shown in Fig. 3, during this one-month period of no treatment, PCB mean concentration levels had a 4% insignificant increase. In contrast, all rescue workers had measurable decreases in these PCBs following treatment. Brominated dioxins, brominated dibenzo-furans, and polybrominated diphenyl ether congeners were at low levels or below the limit of detection (data not shown).

Subjects reported a similar pattern of health complaints and manifested symptoms including respiratory impairment, mental/emotional distress (two met PTSD criteria), decreased sensory systems, chronic muscle and joint pain, gastrointestinal disorders, and skin rashes. These symptoms were completely resolved or were satisfactorily improved on completion of treatment. The neurophysiological test results also improved. Fig. 4 shows the change in mean severity of self-reported symptoms as measured by a questionnaire.

#### 4. Discussion

In view of the documented persistence of adverse health effects in individuals exposed during the collapse of the WTC, it is important to not only document symptoms and possible causes but to identify workable treatment

Table 1

Measured dioxin, dibenzoluran, and polychlorinated bipner	ıran, anu 🏻	oolychloru	nated orpn	enyl levels	lyl levels" before and after treatment of WTC-exposed individuals, INT 2004	nd arter ti	eatment c	. w 1 C-ey	posed ma	IVIduals, 1	NY 2004					
Identification	MTO	WTC002	WTC005	3005	WTC006	900;	WTC009	600;	WTC011	:011	WTC	WTC013	<sub>q</sub> 20905H	305 b	Comparison NHANES III	arison ES III
Congener	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	LOD	75th
2.3.7.8-Tetra-CDD	1.9	1.3	3.2	2.1	2,2	1.8	1,4	1.7	3.0	1.4	1.6	1,6	2.6	2.0	4.8 pg/g	n.d.
1.2.3.7.8-Penta-CDD	5.3	4.1	7.1	7.0	8.1	7.3	5.8	7.1	4.1	3.5	4.1	2.7	6.3	6.2	5.3	n.d.
1.2.3.4.7.8-Hexa-CDD	4.0	3.5	6.5	2.6	6.1	4.8	2'8	6.3	2.4	n d (2)	n.d.(4)	n d (4)	9	9.6		
1.2.3.6.7.8-Hexa-CDD	31	29	38	35	49	44	33	40	20	14	15	16	41	36	7.5	36.1
1.2.3.7.8.9-Hexa-CDD	2.8	3.4	9.5	5.9	5.1	6.2	4.0	8'5	5.4	3.4	n.d.(3)	(e) p u	9'5	6.3	9.7	n.d.
1.2.3.4.6.7.8-Hepta-CDD	56	27	26	54	48	42	51	63	21	56	24	25	47	55	24.7	61.9
OCDD	94	92	272	250	437	426	195	242	99	79	134	114	186	251	145	445
2.3.7.8-Tetra-CDF	n.d.(1)	n d (1)	1.2	1.2	n d (1)	n d (1)	n d (1)	n d (1)	n.d.(1)	n d (1)	1.3	1.4	1.3	1.4	4.6	n d
1.2.3.7.8-Penta-CDF	n.d.(1)	n d (1)	1.3	1.3	n d (1)	n d (1)	n.d.(1)	n d (1)	n.d.(1)	n d (1)	1.1	1.1	1.9	1.9	2	n d
2.3.4.7.8-Penta-CDF	3,4	4.0	10.3	8.6	7.7	6'2	4.7	0'9	3.5	2.9	9'9	6.3	9.1	10	4.8	n d
1.2.3.4.7.8-Hexa-CDF	4.3	4.7	9.2	8.8	8.2	6.8	7.3	7.3	3.8	4.2	0'9	99	10.4	13	4.7	n d
1.2.3.6.7.8-Hexa-CDF	3.2	3.4	7.0	7.1	7.5	9.9	3.9	6.1	2.3	3.3	4.8	9.5	7.2	10	4.8	n d
1.2.3.7.8.9-Hexa-CDF	n d (1)	n.d.(1)	n.d.(1)	n d (1)	n d (1)	n.d.(2)	n d (1)	n d (2)	n d (2)	n d (2)	n.d.(3)	n.d.(3)	n.d.(5)	n d (5)	4.6	n.d.
2.3.4.6.7.8-Hexa-CDF	1.4	n d (2)	3.5	2.7	2.3	1.5	2.5	2.1	1.6	n d (1)	5.4	5.4	2.1	6.0	4.8	n d
1.2.3.4.6.7.8-Hepta-CDF	3.1	2.7	4.8	5.5	2.7	6.5	5.9	8.3	3.6	2.0	2.5	4.4	6.1	6.8	2.2	n.d.
1.2.3.4.7.8.9-Hepta-CDF	n.d.(2)	n.d.(1)	n d (1)	n d (2)	n d (1)	n d (3)	n.d.(1)	n d (2)	n.d.(2)	n d (3)	n d (5)	n d (5)	рu	n d (8)		
OCDF	n d (4)	n d (3)	n.d (3)	n d (5)	n d (3)	n d (10)	n d (4)	n d (5)	n d (6)	n d (11)	n d (22)	n d (24)	n d	n d (33)	12.6	n d
	n d (14)	n.d.(24)	n.d.(13)	n d (17)	n.d.(12)	n.d.(22)	n.d.(18)	n.d.(27)	n d (17)	n.d.(23)	n d (26)	n.d.(28)	.89	n.d.(31)		
3,4,4',5-TCB (81)	n.d.(2)	2.6	2.5	3.8	n.d.(2)	2.4	2.4	4.6	n.d.(3)	3,3	5.2	0.6	12.0	6	25.8	n.d.
3,3,4,4,5-PeCB (126)	23	28	44	41	64	65	41	44	20	14	36	39	197	163	6	n d
3,3,4,4,5,5-HxCB (169)	21	28	23	23	48	49	26	43	23	16	31	28	51	56	6.6	n d
2,3,3,4,4'-PeCB (105)	1203	1006	7908	5222	537	443	4050	3626	1881	1184	1782	1886	41765	31469	6400	n.d.
2,3,4,4',5-PeCB (114)	675	581	1906	1380	1253	1000	980	887	771	500	1236	1289	17746	13986	6400	n.d.
2,3',4,4',5-PeCB (118)	6153	4955	31225	22656	4665	3266	20163	16772	9408	5355	10062	9705	207921	152910	6400	14700
2',3,4,4',5-PeCB (123)	232	234	492	556	283	227	245	421	149	174	310	373	1900	2853		
2,3,3,4,4,5-HxCB (156)	8045	6807	6987	4598	9759	7214	6478	6403	7501	4290	9977	9371	95751	66304	6400	n.d.
2,3,3,4,4,5'-HxCB (157)	1596	1548	1396	1086	2042	1606	1480	1523	1550	1003	2485	2293	18706	16126	6400	n.d.
2,3,4,4,5,5-HxCB (167)	756	798	2029	1601	1096	911	1683	1802	1047	2123	1918	1867	18881	16344	6400	n.d.
2,3,3,4,4,5,5-HpCB (189)	531	629	475	430	952	955	594	062	523	413	846	738	2324	2336		
Total PCDDs/PCDFs	180	177	424	396	287	562	320	395	136	142	210	193	333	416.1		
Total non-ortho-PCBs	44	58	20	89	112	116	20	91	43	33	72	9/	328	229		
Total mono-ortho-PCBs	19191	16558	52417	37530	20587	15623	35673	32223	22832	15042	28616	27521	404994	302328		
Total WHO-TEQ PCDDs/PCDFs	13.9	12	23.1	21	22.4	21	15.8	19	12.7	9.1	13	41	21	22		
Total WHO-TEQ non-ortho- PCBs	8.4	3.1	13.8	4.3	14.0	7.0	11.3	4.8	8.4	1.6	6'8	4.2	111.9	17		
Total WHO-TEQ mono-ortho- PCBs	22.3	5.2	37	6.4	36.5	5.4	27.1	9'9	21	3.6	8.2	8.2	133,3	67		

<sup>a</sup> Values in pg/g (ppt), lipid based; Samples from Human Blood.

<sup>b</sup> Patient H 5-0605 blood tested in 5/2003 [firefighter sent us his PCB value of 32ppb (Webb and McCall) on 1/9/02].

NHANES III data from Second National Report on Human Exposure to Environmental Chemicals. US Dept of Health and Human Services NCEH Pub. No. 02-0716

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Table 2
Mean and median differences for PCDDs, PCDFs and PCBs following detoxification

Congener	Mean difference	Median difference	(p-value)
2.3.7.8-Tetra-CDD	0.57	0.60	0.06
1.2.3.7.8-Penta-CDD	-0.02	0.10	0.94
1.2.3.4.7.8-Hexa-CDD	0.14	0.51	0.56
1.2.3.6.7.8-Hexa-CDD	1.65	2.57	0.38
1.2.3.7.8.9-Hexa-CDD	-0.37	-0.61	0.44
1.2.3.4.6.7.8-Hepta-CDD	-2.70	-1.38	0.38
OCDD	-10.48	-0.99	0.69
2.3.7.8-Tetra-CDF	-0.03	0.00	0.5
1.2.3.7.8-Penta-CDF	-0.001	0.00	0.99
2.3.4.7.8-Penta-CDF	23	-0.24	0.58
1.2.3.4.7.8-Hexa-CDF	-0.32	-0.37	0.47
1.2.3.6.7.8-Hexa-CDF	-0.32	-0.37	0.47
1.2.3.7.8.9-Hexa-CDF	*	*	*
2.3.4.6.7.8-Hexa-CDF	0.15	0.75	0.44
1.2.3.4.6.7.8-Hepta-CDF	-0.62	-0.70	0.22
1.2.3.4.7.8.9-Hepta-CDF	*		*
OCDF	*	*	*
3,3',4,4'-TCB (77)	9.71	0.00	0.99
3,4,4′,5-TCB (81)	-1.66	-2.19	0.16
3,3',4,4',5-PeCB (126)	4.39	-1.31	0.69
3,3',4,4',5,5'-HxCB (169)	-2.76	-0.73	0.47
2,3,3',4,4'-PeCB (105)	2041.47	423.78	0.05
2,3,4,4',5-PeCB (114)	706.42	253.28	0.03
2,3',4,4',5-PeCB (118)	10568.20	3391.45	0.02
2',3,4,4',5-PeCB (123)	-175.35	-63.00	0.08
2,3,3',4,4',5-HxCB (156)	5644.41	2388.82	0.02
2,3,3',4,4',5'-HxCB (157)	581.48	310.29	0.03
2,3',4,4',5,5'-HxCB (167)	280.59	51.00	0.58
2,3,3',4,4',5,5'-HpCB	-6.55	-2.96	0.99
(189)			
Total PCDDs/PCDFs	-12.86	3.03	0.94
Total non-ortho-PCBs	9.61	-4.00	0.81
Total mono-ortho-PCBs	19640.66	4963.62	0.02

Wilcoxon Rank Test.

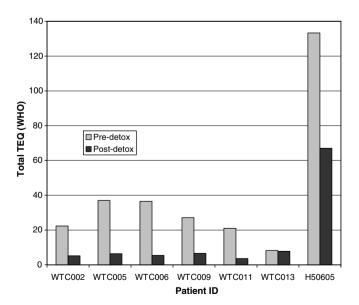


Fig. 1. Changes in Blood Total WHO-TEQ Mono-Ortho PCB Levels with Detoxification.

modalities. The purpose of characterizing the levels of these compounds was to determine whether compounds of this

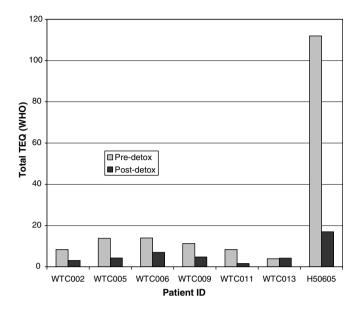


Fig. 2. Changes in Total WHO-TEQ Non Ortho PCB Levels with Detoxification.

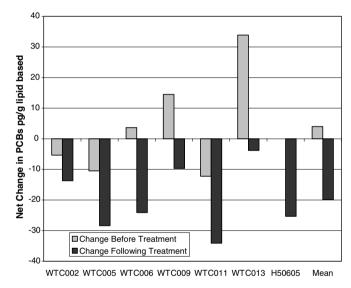


Fig. 3. Change in Mono-Ortho PCB Levels with Treatment Compared with One Month of No Treatment.

class could be detected in this population this long after exposure. Additionally, assuming detection, we wanted to know whether their levels could be reduced by detoxification treatment. It is useful to have a marker compound for use in future studies that plan to evaluate the use of this treatment method.

This was a complex exposure involving many different compounds and under many different circumstances. Various reports suggest that PCBs, PCDDs, PCDFs and brominated flame retardants were not above background in the dust at the WTC site when tested 5–6 days after the attack. However the large volume of polybrominated biphenyls and brominated diphenyl ethers could have led to significant ambient exposure during the first few days after the colapse (Lioy et al., 2002). These compounds have

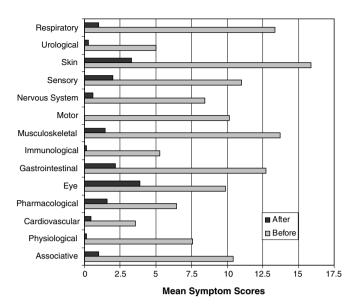


Fig. 4. Self Reported Symptom Severity Before and After Detoxification.

long half-lives. (Schecter et al., 2002a; Schecter et al., 2002b) It is unclear why PCBs but not PCDDs, PCDFs or brominated flame retardant levels were elevated, despite previous positive findings in chemical workers decades after exposure. (Sullivan and Krieger, 1991) We can only measure elevated levels of PCBs and dioxins in the human body if uptake increases body burden significantly. For comparison: the intake via food ranges between 50 and 100 pg TEQ/day. A typical air concentration may be at 0.05 pg TEQ/m<sup>3</sup>. Even at a 1000 times elevated air concentration, 24 h inhalation (20 m<sup>3</sup>) adds "only" 1000 pg to the body burden (equivalent to about 10 days additional uptake from food).

The elevated concentrations of the PCB congeners found in some rescue workers appear to be consistent with the several dozen firefighters tested by FDNY and noted to have elevated PCB levels above 12 PPB (as reported by Medilabs, Valley Cottage NY – under contract with the New York City Fire Department Medical Department.). This level was found by using the Webb and McCall technique, which averages 6 ppb in the general population. These levels are considerably higher than would be expected in the general population, and consistent with levels seen in occupational exposure to PCBs. (Edelman et al., 2003) A particular firefighter (Patient HB50605) provided us with results of two prior FDNY-ordered PCB tests (based on Arochlor 1260, Webb and McCall technique). Test results were 32 ppb on January 9th, 2002 and 13 ppb on September 9th, 2002. He had his blood drawn and it was analyzed for dioxin, dibenzofuran and PCB at ERGO laboratory on May 2003 (Table 2). Using a more reliable and sensitive technique, his levels measured 416 ppb (WHO-TEQ 133.3). This firefighter (Patient H 5-0605) had also worked on the day of and several days following the collapse.

A study by Edelman et al, reports an unanticipated increase in heptachlorodibenzodioxin and heptachlorodibenzofuran, associated with exposure from the WTC collapse (Edelman et al., 2003). However, the authors do not presume the exposure to be from the WTC collapse alone.

The symptoms presented by the seven men in this group matched the pattern seen in studies of WTC-exposed populations. (Levin et al., 2004) A 2003 Mt. Sinai/NIOSH/CDC analysis of 250 WTC screening program participants document that approximately half of the sample had persistent WTC-related pulmonary, ENT and/or mental health symptoms that persisted a year following exposure (Grandjean, 2003). The persistent symptomatology and its successive improvements with detoxification is consistent with medical records from the nearly 400 WTC-exposed men and women who completed detoxification treatment.

This pilot study is limited by its small sample size. No relationships can be inferred between the PCB contamination found and the observed symptoms, or between reduction in these levels and the improvements following treatment. However, it is interesting that studies evaluating the adverse effects of high levels of PCB exposure commonly list neurologic, (Chen et al., 1985; Chia and Chu, 1984) immune and neuroendocrine effects (Carpenter, 1998), neurobehavioral effects, (Brown and Nixon, 1979; Schantz et al., 2001) rashes and acne, nausea and other gastrointestinal problems (Agency for Toxic Substances and Disease Registry (ATSDR, 2000)). Occupational studies suggest that exposure to PCBs may also cause irritation to the nose and lungs, blood and liver changes, fatigue, and depression. Furthermore, previous studies of PCB-exposed firefighters have demonstrated neurologic symptom improvement on completion of this treatment. (Kilburn et al., 1989) Prior studies using this method of detoxification showed reduced body burden of PCBs, PBBs and chlorinated pesticides (Schnare et al., 1984). The data presented here will be used for a larger subsequent study where correlations may be further tested. Even three years after the WTC attacks, thousands of exposure victims continue to have persistent illness. New approaches to this public health predicament are urgently needed.

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