

Performance of a high flow rate, thermally-extractable denuder for atmospheric semivolatile organic compound concentration measurement

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20 **Procedure for coating denuders with polydimethylsiloxane** 21 **(PDMS)**

22 The denuders were coated with PDMS (RTX-1, Restek). A 0.1 g mL^{-1} solution of PDMS was
23 prepared in a 1-L volumetric flask by dilution with pentane (B&J 99.9 %, VWR). Dicumyl
24 peroxide (98 %, Sigma-Aldrich) was added to the pentane solution at 2.5 mg mL^{-1} as a
25 crosslinking agent just prior to coating. Denuders were coated in a dry glovebox ($< 10 \%$ relative
26 humidity). Prior to coating, denuders were heated under flowing helium ($320 \text{ }^{\circ}\text{C}$, 20 min.) to
27 remove adsorbed moisture, then transferred into the glovebox without exposure to the
28 atmosphere. Helium (99.999 %) was purified using a water, oxygen, and hydrocarbon trap
29 (RMSHY-4, Agilent Technologies). Denuders were dipped into the PDMS solution. Excess
30 solution was blown out of the honeycomb cells with a jet of nitrogen. Two dips were needed to
31 obtain the target $5\text{-}\mu\text{m}$ coating thickness, determined by mass gain and an estimated surface area
32 of 1.48 m^2 for the 51-mm deep honeycomb. PDMS was removed from the outside surface of the
33 honeycomb by wiping with a pentane-soaked tissue. Denuders were cured under flowing helium
34 (2 L min^{-1}) in a stainless steel foil bag for 20 min. at room temperature, 2 hr. at $40 \text{ }^{\circ}\text{C}$, 1.5 hr. at
35 $140 \text{ }^{\circ}\text{C}$, 12-16 hr. at $320 \text{ }^{\circ}\text{C}$, and cooled under helium purge. To remove non-crosslinked
36 polymer residue, each honeycomb was placed in a metal can with 750 mL of dichloromethane
37 (B&J 99.9 %, VWR Scientific), then turned end-over-end for ten minutes. Excess solution was
38 removed with a jet of nitrogen. Prior to use, denuders were thermally extracted and checked for
39 blank response levels. Denuders were stored in sealed metal cans that had been combusted in air
40 at $450 \text{ }^{\circ}\text{C}$ for 6 hr.

Table S1: Concentration of atmospheric persistent, bioaccumulative, and toxic chemicals
(pg m⁻³ at 25 °C, 1 atm.)^a.

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI		Houghton, MI	
Date		19 May 2008		24 25 Jun. 2008		17 Jul. 2008		29 Jul. 2008		5 Aug. 2008	
Volume, m ³		56.8	59.0	67.9	76.8	109.4	111.6	73.1	70.1	66.3	
Temp., °C		4.5	4.5	11.8	20.0	13.6	13.6	24.9	24.1	24.1	
Rel. humidity, %		79.3	79.3	94.6	74.2	99.7	99.7	71.8	52.5	52.5	
Analyte or co-eluting analyte group	MDL, pg	Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³	
PCB 4 + 10	29.5	<0.5	<0.5	<0.4	1.4		0.7	<0.4	<0.4	<0.4	
PCB 9	19.8	1.0	1.4	<0.3	<0.3	<0.2	<0.2	3.2	<0.3	<0.3	
PCB 7	24.0	<0.4	<0.4	<0.4	<0.3	<0.2	<0.2	<0.3	<0.3	<0.4	
PCB 6	22.1	<0.4	<0.4	6.6	10.9	10.1	7.9	5.1	6.1	6.8	
PCB 5	15.4	<0.3	<0.3	<0.2	0.5	<0.1	<0.1	<0.2	<0.2	<0.2	
PCB 8	37.1	<0.7	<0.6	2.2	12.2	0.9	0.7	2.2	4.1	4.1	
HCB	9.3	55.7	69.2	68.5	95.9	104.9	78.0	66.4	66.7	69.0	
PCB 18	49.0	<0.9		7.6	19.2	4.1	2.6	5.6	9.0	9.0	
PCB 17	10.7	<0.2	<0.2	2.0	6.5	1.0	0.8	2.0	3.4	3.3	
PCB 12	20.2	<0.4	<0.3	<0.3	<0.3	<0.2	<0.2	<0.3	<0.3	<0.3	
PCB 27 + 13	26.2	<0.5	<0.4	<0.4	<0.3	0.3	<0.2	0.4	0.6	0.8	
PCB 24	8.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	
PCB 16	8.6	<0.2	<0.1	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 15	25.5	0.6	<0.4	<0.4	<0.3	<0.2	<0.2	<0.3	<0.4	<0.4	
PCB 32	9.2	<0.2	<0.2	0.6	<0.1	0.5	<0.1		<0.1	2.5	
PCB 54	23.3	<0.4	<0.4	<0.3	<0.3	<0.2	2.4	<0.3	<0.3	<0.4	

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI	Houghton, MI
Date		19 May 2008		24 25 Jun. 2008		17 Jul. 2008		29 Jul. 2008	5 Aug. 2008
PCB 34	14.8	<0.3	<0.3		0.8	<0.1	<0.1	<0.2	<0.2 0.6
PCB 29	17.0	<0.3	<0.3	<0.2	5.1	<0.2	<0.2	<0.2	<0.2 <0.3
PCB 26	13.3	<0.2	<0.2	0.5	<0.2	<0.1	<0.1	0.5	<0.2 1.2
PCB 25	8.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.4 0.5
PCB 31 + 53	22.1	<0.4	<0.4	2.1	13.1	<0.2	0.8	2.0	<0.3 7.2
PCB 28	9.8		<0.2	1.5	8.6	0.7	0.5	1.4	<0.1 5.2
PCB 33 + 20	28.0	<0.5	<0.5	1.1	6.0	0.4	<0.3	0.9	<0.4 <0.4
PCB 51	21.5	<0.4	<0.4	<0.3	0.7	<0.2	<0.2	<0.3	<0.3 <0.3
PCB 45	44.8	<0.8	<0.8	<0.7	10.8	<0.4	<0.4	<0.6	<0.6 1.0

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Table S1: (continued)

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI		Houghton, MI	
Date		19 Apr. 2008		24 25 June 2008		17 Jul. 2008		29 Jul. 2008		5 Aug. 2008	
Analyte or co-eluting analyte group	MDL, pg	Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³	
PCB 22	57.1	<1.0	<1.0	0.7	4.2	<0.5	<0.5	1.3		3.0	2.9
PCB 46	11.0	<0.2	<0.2		0.6	<0.1		<0.2		<0.2	0.3
PCB 73	7.5	<0.1	<0.1	<0.1	<0.1		<0.1	<0.1		<0.1	<0.1
PCB 69	34.3	<0.6	<0.6	<0.5	<0.4	<0.3	<0.3	<0.5		<0.5	<0.5
PCB 52	11.6	<0.2	<0.2	1.1	6.3	<0.1	<0.1	1.1		<0.2	3.7
PCB 48	12.9	5.9	<0.2	<0.2	<0.2	4.1	3.5	<0.2		<0.2	0.5
PCB 49	51.5	<0.9	<0.9	<0.8	4.4	<0.5	<0.5	<0.7		3.3	3.3
PCB 75	36.8	<0.6	<0.6	<0.5	<0.5	<0.3	<0.3	<0.5		<0.5	<0.6
PCB 44	37.0	<0.7	<0.6	1.1	6.6	0.8	0.4	<0.5		3.8	<0.6
PCB 59 + 42	12.8	<0.2	0.4	0.7	3.3	0.3	<0.1	1.0		2.2	2.1
PCB 35	5.7	<0.1	0.4		0.4	0.3	<0.1	0.2		<0.1	<0.1
PCB 71	15.0	<0.3	<0.3		1.3	<0.1	<0.1	<0.2		1.8	1.7
PCB 41	7.5	<0.1	<0.1	0.3	0.9	<0.1	<0.1	0.2		<0.1	<0.1
PCB 64	7.0	<0.1	0.2	0.4	2.6	0.3	0.2	0.6		1.8	1.8
PCB 40 + 37 + octachlorostyrene	13.7	0.5	0.8	1.0	2.5	1.1	0.7	1.5		<0.2	1.6
PCB 103	8.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1		<0.1	<0.1
PCB 100	11.4	<0.2	<0.2	<0.2	<0.1	<0.1	<0.1	<0.2		<0.2	<0.2
PCB 67	11.8	<0.2	<0.2	<0.2	<0.2	<0.1	<0.1	<0.2		0.3	<0.2
PCB 93 + 63	26.2	<0.5	<0.4	<0.4	<0.3	<0.2	<0.2	<0.4		<0.4	<0.4
PCB 95	11.6	<0.2	0.3	1.4	7.8	0.5		1.3		5.2	5.5
PCB 74	7.9	0.2	<0.1	0.3	1.8	<0.1	0.2	<0.1		<0.1	<0.1

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI	Houghton, MI	
Date		19 Apr. 2008		24 25 June 2008		17 Jul. 2008		29 Jul. 2008	5 Aug. 2008	
PCB 70	9.9	<0.2	<0.2	1.2	6.3	0.2	<0.1	<0.1	1.0	1.8
PCB 91 + 66	61.4	<1.1	<1.0	<0.9	<0.8	<0.6	<0.6	<0.8	<0.9	<0.9
PCB 84 + 92 + 56	26.8	<0.5	<0.5	0.9	<0.3	<0.2	<0.2	<0.4	2.8	<0.4
PCB 60 + 101 + 90	22.4	<0.4	<0.4	1.1	6.0	<0.2	<0.2	<0.3	<0.3	4.3
PCB 99	6.1	<0.1	<0.1	0.4	2.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 119 + 83	14.0	<0.2	<0.2	<0.2	0.8	<0.1	<0.1	<0.2	0.2	0.3
PCB 97	32.5	<0.6	<0.6	0.6	<0.4	<0.3	<0.3	<0.4	<0.5	<0.5
PCB 87	11.3	0.4	<0.2	<0.2	0.7	1.9	0.5	<0.2	<0.2	<0.2
PCB 136	12.1	<0.2	0.4	0.3	0.3	1.0	<0.1	7.5	4.6	5.0
PCB 117	10.6	<0.2	<0.2	1.1	2.6	<0.1	<0.1	<0.1	0.5	0.5
PCB 115	9.0	<0.2	<0.2	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 85	7.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table S1: (continued)

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI	Houghton, MI	
Date		19 Apr. 2008		24 25 June 2008		17 Jul. 2008		29 Jul. 2008	5 Aug. 2008	
Analyte or co-eluting analyte group	MDL, pg	Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³	Conc., pg m ⁻³	
PCB 154	9.1	0.2	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 110	8.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 81	9.2	<0.2	<0.2	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1
PCB 82	10.2	<0.2	0.3	<0.2		<0.1	0.1	<0.1	0.3	1.0
PCB 151	14.2	<0.3	<0.2	1.1	1.6	<0.1	<0.1	<0.2	<0.2	<0.2
PCB 135	7.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.6	0.4
PCB 77	8.8	<0.2	<0.1		0.6	<0.1	0.6	<0.1	<0.1	<0.1

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI		Houghton, MI	
Date		19 Apr. 2008		24 25 June 2008		17 Jul. 2008		29 Jul. 2008		5 Aug. 2008	
PCB 144	7.9	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 147	8.5	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 149	10.2	<0.2	0.4	0.6	2.7	<0.1	<0.1	1.0	<0.1	3.1	
PCB 124	7.4	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1	0.5	
PCB 123 + 107	19.9	<0.3	<0.3	<0.3	0.3	<0.2	<0.2	<0.3	<0.3	<0.3	
PCB 134	11.4	<0.2	<0.2	<0.2	0.4	<0.1	<0.1	<0.2	0.2	0.4	
PCB 131 + 118 + PBDE 28	93.0	<1.6	<1.6	1.7	4.1	2.0	<0.8	2.2	<1.3	<1.4	
PCB 122	9.4	<0.2	<0.2	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	
PCB 165	8.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 114 + 146	15.6	<0.3	<0.3	<0.2	0.3	<0.1	<0.1	<0.2	0.4	0.4	
PCB 132	8.3	<0.1	<0.1	0.2	1.1	0.2	0.1	0.3	1.0	1.0	
PCB 153	8.5	<0.2	0.3	0.3	1.5	0.4	0.2	0.5	2.0	1.9	
PCB 179	9.4	<0.2	<0.2	<0.1	0.2	<0.1	<0.1	<0.1	0.3	0.3	
PCB 105	13.9	<0.2	<0.2	<0.2	1.0	0.3	0.2		1.0	0.9	
PCB 141	8.3			<0.1	0.5		<0.1	0.2	0.5	0.5	
PCB 176	11.7	<0.2	<0.2	<0.2	<0.2	<0.1	<0.1	<0.2	<0.2	<0.2	
PCB 137	8.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	
PCB 130	10.3	<0.2	<0.2	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	
PCB 164	7.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 138	10.0	<0.2	<0.2	0.3	1.6	0.4	0.3	0.5	2.1	1.9	
PCB 163 + 129	15.3	<0.3	<0.3	<0.2	0.4	<0.1	<0.1	<0.2	0.5	0.4	
PCB 178	8.6	<0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 158	6.4	<0.1	<0.1	<0.1	0.2	0.1	0.1	0.1	0.3	0.2	
PCB 175	6.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	

Sample location		Eagle Harbor, MI		Houghton, MI 24 25 June 2008		Eagle Harbor, MI 17 Jul. 2008		Eagle Harbor, MI 29 Jul. 2008	Houghton, MI 5 Aug. 2008
Date		19 Apr. 2008		June 2008		17 Jul. 2008		29 Jul. 2008	5 Aug. 2008
PCB 187	7.3	<0.1	<0.1	<0.1	0.4	0.1	0.1	0.2	0.7 0.7
PCB 128	7.2	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	0.4 0.3

Table S1: (continued)

Sample location		Eagle Harbor, MI		Houghton, MI		Eagle Harbor, MI		Eagle Harbor, MI		Houghton, MI	
Date		19 Apr. 2008		24 25 June 2008		17 Jul. 2008		29 Jul. 2008		5 Aug. 2008	
Analyte or co-eluting analyte group	MDL, pg	Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³		Conc., pg m ⁻³	
PCB 185	7.5	<0.1	<0.1	<0.1	0.2	0.2	0.2	0.4			
PCB 174	10.5	<0.2	<0.2	<0.2	0.3	<0.1	<0.1	<0.1	0.4	0.4	
PCB 167	9.6							0.6	<0.1	<0.1	
PCB 202	13.6			<0.2	<0.2	<0.1		<0.2	0.7	0.8	
PCB 177	7.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	
PCB 173	5.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 156	6.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	
PCB 172	10.1	<0.2	1.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	
PCB 157	7.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 180	7.3	0.3	0.4	<0.1	0.3	<0.1	<0.1	0.1	0.6	0.5	
PCB 193 + 200	15.9	<0.3	<0.3	<0.2	<0.2	<0.1	0.2	<0.2	<0.2	<0.2	
PCB 191	36.2	<0.6	<0.6	<0.5	<0.5	<0.3	<0.3	<0.5	<0.5	<0.5	
PCB 170	7.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.1	
PCB 199	7.2	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.2	0.2	
PCB 190	6.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 196	8.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	
PCB 203	6.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 208	6.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
PCB 189	31.9	<0.6	<0.5	<0.5	<0.4	<0.3	<0.3	<0.4	<0.5	<0.5	
PCB 195 + 207	35.7	<0.6	<0.6	<0.5	<0.5	<0.3	<0.3	<0.5	<0.5	<0.5	
PCB 194 + PBDE 100	30.9	<0.5				1.9	2.2			12.2	

Sample location		Eagle Harbor, MI		Houghton, MI 24 25 June 2008		Eagle Harbor, MI 17 Jul. 2008		Eagle Harbor, MI 29 Jul. 2008	Houghton, MI 5 Aug. 2008	
PCB 205	6.4	<0.1	<0.1	<0.1	<0.1	<i>0.2</i>	<i>0.2</i>	<i>0.4</i>	<0.1	<i>0.7</i>
PCB 206	6.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PCB 209	22.5	<0.4	<0.4	<0.3	<0.3	<0.2	<0.2	<0.3	<0.3	<0.3

^a Observations that fell between the MDL and QL are given in italicized font. In the case of non-detect, the MDL is given in boldface font preceded by the symbol "<". Missing values indicate observations that failed the blank criterion. PBDE 47 and 99 were included as analytes but were not reported because of persistent blank failures. PBDE 28 and 100 are indicated as co-eluting interferences with analytes, but were not included in the calibration standards. Air temperature and relative humidity are means over the sample collection period.

Table S2: Paired analyte groups for comparison of concentrations measured by high-flow denuder to IADN Project high-volume samples.

High-flow denuder	IADN Project	High-flow denuder	IADN Project
PCB 4 + 10	4 + 10	PCB 91 + 66	66 ^b
PCB 9	7 + 9 ^a	PCB 84 + 92 + 56	92 + 84 ^b
PCB 6	6	PCB 60 + 101 + 90	101 ^b
PCB 8	8 + 5 ^a	PCB 99	99
HCB	HCB	PCB 119 + 83	83 ^b
PCB 18	18	PCB 97	97
PCB 17	15 + 17 ^a	PCB 87	87
PCB 12	12	PCB 85	85
PCB 27 + 13	13 ^b	PCB 110	110
PCB 16	16	PCB 81	81
PCB 32	32	PCB 135	135 + 144 ^a
PCB 26	26	PCB 77	77
PCB 31 + 53	31 ^b	PCB 149	123 + 149 ^a
PCB 28	28	PCB 114 + 146	114 ^b
PCB 33 + 20	33 ^b	PCB 132	132 + 153 + 105 ^a
PCB 45	45	PCB 138	163 + 138 ^a
PCB 22	22	PCB 128	128
PCB 52	52	PCB 174	174
PCB 48	48	PCB 156	156
PCB 49	49	PCB 172	172
PCB 59 + 42	42 ^b	PCB 157	157
PCB 71	41 + 71 ^a	PCB 180	180
PCB 64	64	PCB 170	170 + 190 ^a
PCB 100	100	PCB 199	199
PCB 95	95	PCB 205	205
PCB 74	74	PCB 206	206
PCB 70	70 + 76 ^a		

^a PCB congeners resolved in the high-flow method were added to match the IADN analyte group.

^b One or two co-eluting congeners in the high-flow method were not included in the IADN method.

Table S3: Between-method bias (high flow – high volume) as a function of relative PCB analyte volatility (GC elution order) and percent of total PCB concentration in air associated with particles over the sampling temperature range.

	Median conc., pg m ⁻³	Median difference, pg m ⁻³	Relative difference, %	n	Percent particle- associated ^a
Earlier-eluting than first tetraCB	2.7	-0.14	-5.1	24	<1
TetraCB	1.8	-0.45	-25.2	21	<1
PentaCB and hexaCB	1.0	-0.48	-45.4	14	3 - <1
Later-eluting than first heptaCB	0.6	-0.27	-48.4	11	32 - 4

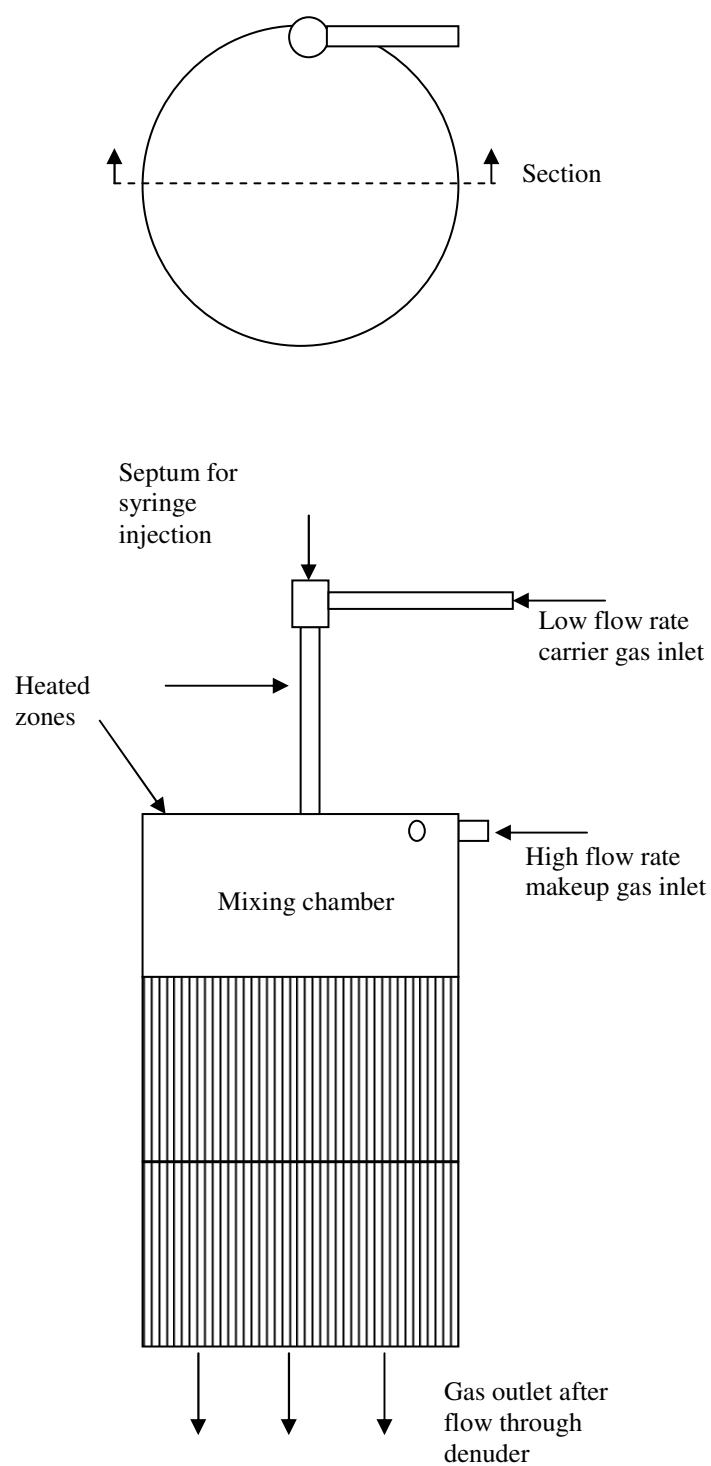
^a Calculated after Harner and Shoeib (1), with K_{oa} for PCBs 18, 52, 101, 180 (2) at 4.5 and 25 °C, 10 µg m⁻³ TSP, and fraction organic carbon of 0.2.

References

- (1) Harner, T.; Shoeib, M., Measurements of octanol-air partition coefficients (K_{OA}) for polybrominated diphenyl ethers (PBDEs): Predicting partitioning in the environment. *J. Chem. Eng. Data.* **2002**, *47*, (2), 228-232.
- (2) Beyer, A.; Wania, F.; Gouin, T.; Mackay, D.; Matthies, M., Selecting internally consistent physicochemical properties of organic compounds. *Environ. Toxicol. Chem.* **2002**, *21*, (5), 941-953.
- (3) Wu, R.; Backus, S.; Basu, I.; Blanchard, P.; Brice, K.; Dryfhout-Clark, H.; Fowlie, P.; Hulting, M.; Hites, R., Findings from quality assurance activities in the Integrated Atmospheric Deposition Network. *J. Environ. Monit.* **2009**, *11*, 277-296.

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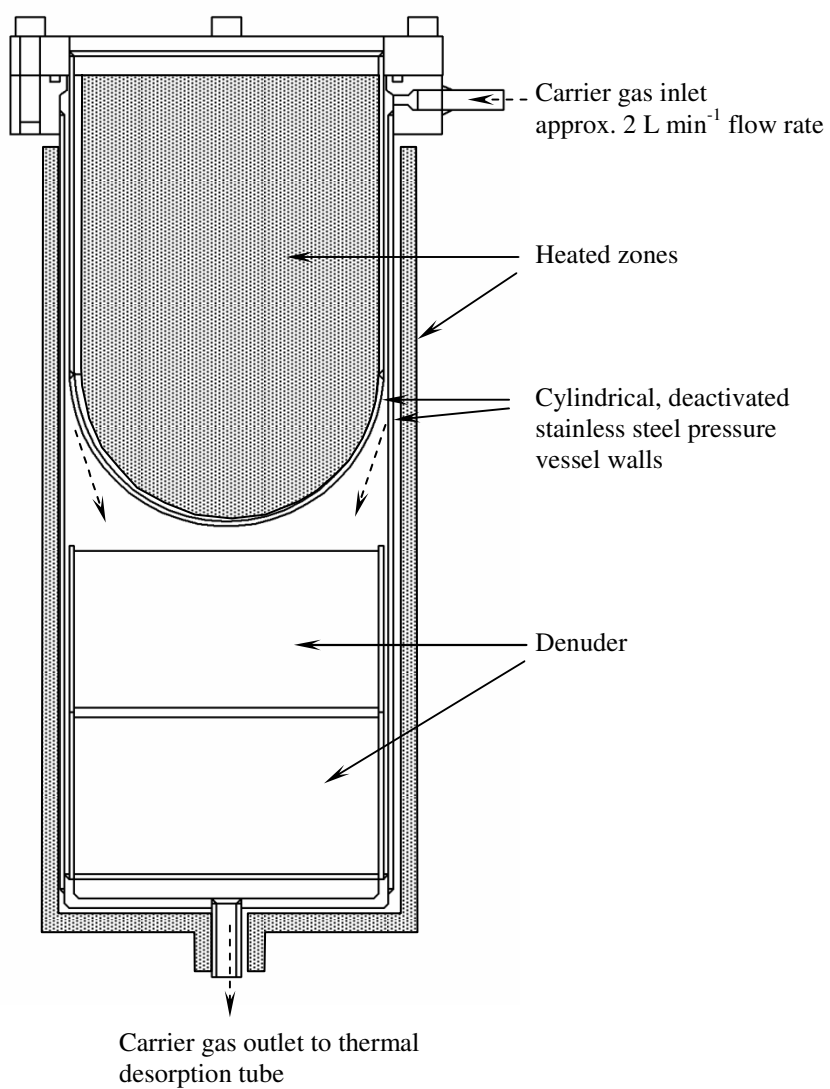
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87 **Figure S1:** Schematic illustration of the high-flow denuder hot-spike device.



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90 **Figure S2:** High-flow denuder sample collection at Eagle Harbor, MI

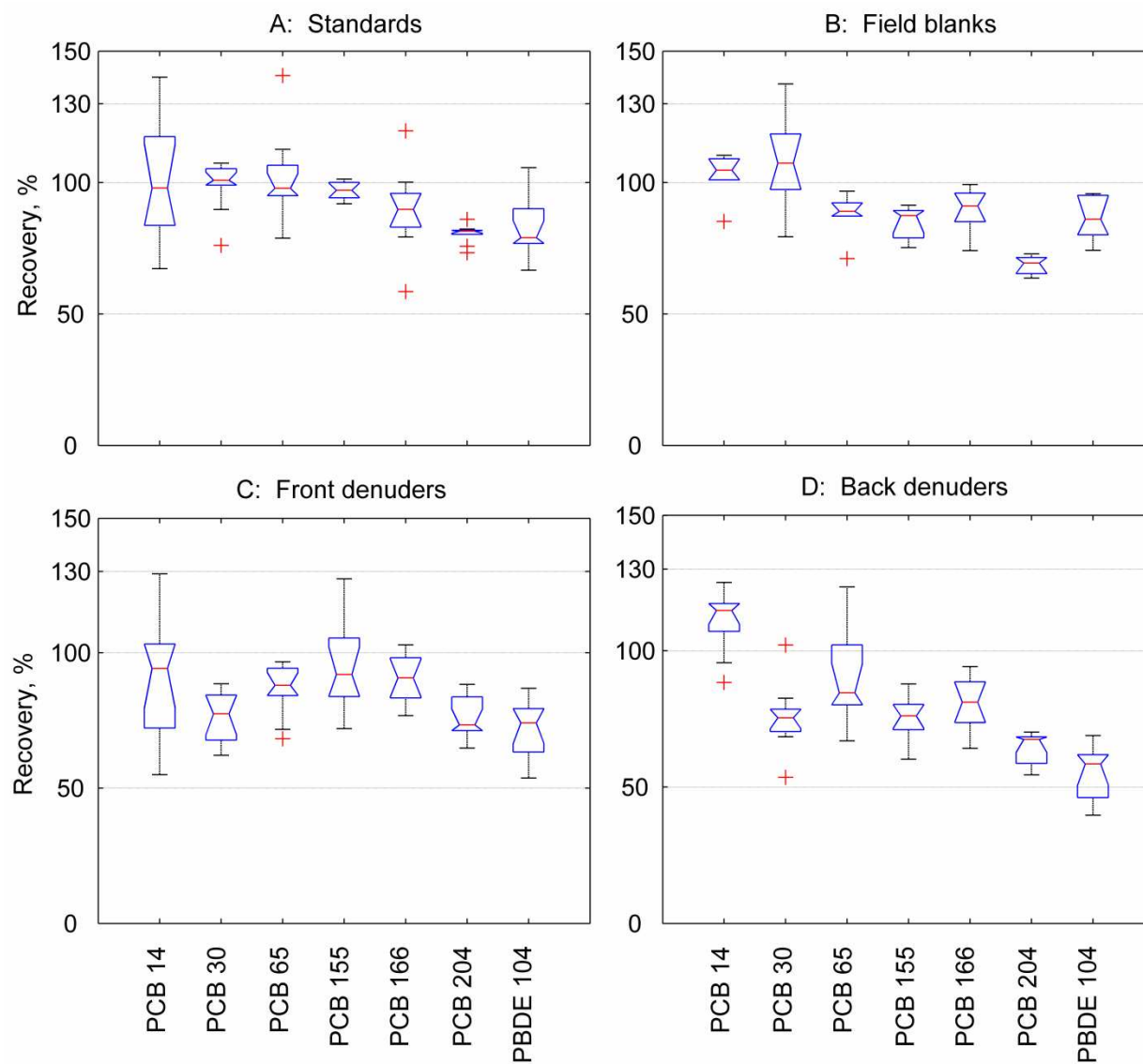


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95 **Figure S3:** Schematic longitudinal cross-section of the analyte transfer apparatus (ATA).



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98 **Figure S4:** Recovery of surrogate standards (PCBs 14, 65, 166, and PBDE 104) hot-spiked into
 99 high-flow denuders with (C, n = 11; D, n = 10) and without (A, n = 10; B, n = 6) subsequent
 100 sample collection, and internal standards (PCBs 30, 155, and 204) hot-spiked subsequent to
 101 sample collection. The y-axis scales were set to indicate data quality objectives for surrogate
 102 recoveries of 50 – 130 % for similar samples collected by high-volume sampler (3).