

Polychlorinated Naphthalenes and Coplanar Polychlorinated Biphenyls in Arctic Air

TOM HARNER,*[†] HENRIK KYLIN,[‡]
TERRY F. BIDDLEMAN,[⊥]
CRISPIN HALSALL,[§]
WILLIAM M. J. STRACHAN,^{||}
LEONARD A. BARRIE,[⊥] AND
PHIL FELLIN[△]

*Chemical Engineering and Applied Chemistry,
University of Toronto, 200 College Street,
Toronto, Ontario M5S 1A4, Canada, Department of
Environmental Assessment, Swedish University of Agricultural
Sciences, P.O. Box 7050, SE-750 07 Uppsala, Sweden,
Atmospheric Environment Service, 4905 Dufferin Street,
Downsview, Ontario M3H 5T4, Canada, Environmental
Science Department, Institute of Environmental and Natural
Sciences, Lancaster University, Lancaster LA1 4YQ, U.K.,
Canada Center for Inland Waters, P.O. Box 5050,
Burlington, Ontario L7R 4A6, Canada, and Conner Pacific,
2 Tippet Road, Toronto, Ontario M3H 2V2, Canada*

Concentrations of polychlorinated naphthalenes (PCNs) are reported for the first time in arctic air. The data represent combined air samples from the Barents Sea ($n = 2$), eastern Arctic Ocean ($n = 10$), Norwegian Sea ($n = 2$), and two land-based monitoring stations at Alert, Canada ($n = 5$), and Dunai Island in eastern Siberia, Russia ($n = 3$). Values for Σ PCN (pg m^{-3}) were 6–49 for shipboard samples and 0.3–8 for land-based stations and were dominated by the 3-Cl and 4-Cl homologues, which accounted for 90–95% of the total mass. Average values for Σ PCB (pg m^{-3}) for the shipboard samples were 126, 24, and 75 for the Barents Sea, eastern Arctic, and Norwegian Sea, respectively. Three-dimensional 5-day air parcel back-trajectories arriving at the ship at 850 and 925 hPa suggested that elevated PCB and PCN concentrations for shipboard samples originated in Europe. Concentrations (fg m^{-3}) of coplanar PCBs in arctic air were 3–40 (PCB 77) and 0.3–8 (PCB 126)—about an order of magnitude lower than in urban air. Higher concentrations of PCB 77 and PCB 126, 347 and 5.0 (fg m^{-3}), respectively, were found in the Barents Sea for two samples with elevated Σ PCBs. The proportion of coplanar PCBs to Σ PCBs was within the range of values reported for Aroclor and Clophen mixtures. The 2,3,7,8-TCDD toxicity of the air samples was assessed in terms of the TEQ (dioxin toxic equivalents) contribution of mono-ortho PCBs (congeners 105, 114, 118, 156), non-ortho (coplanar) PCBs (congeners 77 and 126), and dioxin-like PCNs for which toxic equivalent factors have been determined. The results show a 13–67% TEQ contribution of PCNs in arctic air, and it is concluded that further investigation of this compound class is merited.

Introduction

Polychlorinated naphthalenes (PCNs) are widespread environmental contaminants that have been reported in a range of environmental media (1, 2) including arctic biota (3, 4). The ubiquitous nature of PCNs is of concern because of their dioxin-like toxicity, which is of similar magnitude to some of the coplanar PCBs (5). Although the use of PCNs has declined in the past few decades, they are not prohibited in most countries and still occur in many PCB-like applications such as capacitor fluids, engine oil additives, and electrical insulators (6). PCNs have also been found in incinerator emissions (7), as contaminants in commercial PCB fluids (8), and have recently been reported in air (9, 10). PCNs were also identified in air samples from northern Sweden but not quantified (11).

Polychlorinated biphenyls (PCBs) are also a concern in the arctic environment. Unlike the PCNs, levels of PCBs in arctic air (12) and biota (13, 14) have been fairly well monitored, especially in the past decade. However, there has only been one report of levels of coplanar PCBs, the most toxic congeners, in air (15). Coplanar PCBs have no ortho-substituted chlorines and are structurally similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. They represent a small fraction of the total PCB mass and often co-elute with more abundant congeners. Consequently, the analysis of coplanar PCBs requires special fractionation procedures (16).

This paper summarizes atmospheric levels of PCNs and coplanar PCBs over the eastern Arctic Ocean and at two land-based arctic monitoring stations (Alert, NWT, Canada and Dunai Island, Russia). Results are compared with urban data on the basis of average concentrations, congener profiles, and relative toxicity contributions.

Experimental Methods

Eastern Arctic Ocean. In the summer of 1996, the Swedish icebreaker *Oden* embarked on a 3-month scientific expedition to the eastern Arctic Ocean (Figure 1, cruise track). A total of 34 air samples was collected using a high-volume train consisting of a glass fiber filter (GFF) followed by two polyurethane foam plugs (PUF) (17). Flow rates were approximately $0.4 \text{ m}^3 \text{ min}^{-1}$. Collection dates and other information are summarized in Table 1.

Previous studies with persistent organic pollutants (POPs) in the Arctic Ocean have shown that most of the chemical mass is associated with the gas phase, especially during summer months (12, 18). Therefore, only the PUF plug values were used to calculate air concentrations. PUF plugs were Soxhlet extracted using petroleum ether, and the volume was reduced to 2 mL by rotary evaporation and nitrogen blow down. Extracts were fractionated on a column of silicic acid overlaid with neutral alumina (19). PCNs and PCBs were eluted in fraction F1 with 30 mL of petroleum ether. Fraction F2, which was not analyzed in this study, was eluted with 25 mL of dichloromethane and contained polycyclic aromatic hydrocarbons and most organochlorine pesticides. To increase detection, several samples were combined in

* Corresponding author present address: Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario M3H 5T4, Canada. Phone: (416) 739-4473; fax: (416) 739-5708; e-mail: tom.harner@ec.gc.ca.

[†] University of Toronto.

[⊥] Atmospheric Environment Service.

[§] Lancaster University.

^{||} Canada Center for Inland Waters.

[‡] Swedish University of Agricultural Sciences.

[△] Conner Pacific.

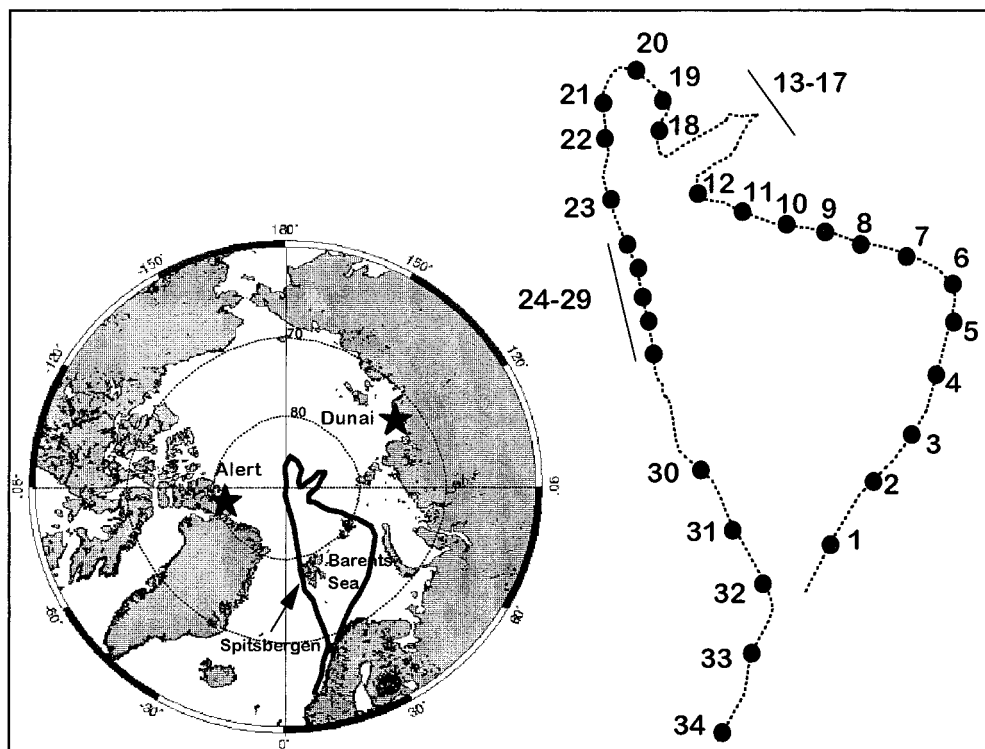


FIGURE 1. Map showing cruise track for the *Oden* 1996 expedition and midpoint locations for arctic air sampling stations.

groups of 2–4, giving a total of 14 representative air samples. The F1 portions were further fractionated on a minicarbon column to separate the mono- and non-ortho PCBs from the multi-ortho congeners. This column consisted of AX-21 activated carbon mixed 1:20 with silicic acid prepared as described by Falconer et al. (20). The first fraction (F1-1) was eluted with 5 mL of 30% dichloromethane in cyclohexane and contained the multi-ortho and a portion of the mono-ortho PCBs. The second fraction (F1-2) was eluted with 5 mL of toluene and contained the PCNs, non-ortho PCBs, and the remainder of the mono-ortho congeners. PCB 103 was added as an internal standard to all samples.

Non-ortho PCBs (congeners 77, 81, 126, 169) and PCNs in fraction F1-2 and mono-ortho PCBs (congeners 105, 114, 118, 156) in fraction F1 were determined by gas chromatography negative ion mass spectrometry (GC–NIMS) on a Hewlett-Packard 5890-MS engine using a 30 m DB-5MS column (0.25 mm i.d., 0.25 μ m film, J&W Scientific). PCBs were quantified against a mixture of non-ortho and mono-ortho PCBs (19). PCNs were quantified against Halowax 1014 (EPA, Research Triangle Park, NC), a commercial mixture of 2-Cl–8-Cl PCNs, using experimentally determined mass percent contributions for each peak (10). Mass percent contributions were determined by gas chromatography (Hewlett-Packard 5890 Plus) with flame ionization detection (GC–FID), which was assumed to respond to the carbon skeleton of the PCN molecule.

Multi-ortho PCBs in fraction F1-1 were determined using a Hewlett-Packard GC equipped with an electron capture detector (GC–ECD). Peaks were separated on a 60 m DB-5MS column (J&W Scientific, 0.25 mm i.d., 0.25 μ m film thickness) operated with hydrogen carrier gas at 50 cm s⁻¹. Sample injections were splitless with split opened after 0.5 min and the injector at 250 °C. The temperature program was 90 °C for 0.5 min, 10 °C min⁻¹ to 160 °C, and 2 °C min⁻¹ to 250 °C with the detector at 250 °C. PCBs were quantified against a mixture of 56 individual congeners (Accustandard, New Haven, CT), and PCB 103 was used as an internal standard.

Prior to Soxhlet extraction, PUF plugs were fortified with a surrogate mixture containing ¹³C₁₂ PCB–congeners 81, 77, 105, 126, and 169. Recoveries of these surrogates were used to correct for non-ortho PCB losses. To correct for PCN and mono-/multi-ortho PCB losses, four clean PUFs were spiked with Halowax 1014 and a PCB mixture containing 56 congeners. These were treated as samples, and recovery values were determined.

Alert and Dunai. The station at Alert has been monitoring air concentrations of persistent organic pollutants since 1992 as part of the Northern Contaminants Program initiated by the federal Department of Indian Affairs and Northern Development, Canada. The Alert station (82.3 N, 62.2 W) is located on Ellesmere Island. At the Russian station, located on Dunai Island in eastern Siberia (74.6 N, 124.3 E), 2 years of sampling was undertaken between March 1993 and summer 1995.

At both locations, weekly air samples were collected at a flow rate of approximately 1.1 m³ min⁻¹ using a high-volume train consisting of a 20 cm diameter glass fiber filter followed by two 20 cm diameter, 4 cm thick PUF plugs. Each weekly sample represented an air volume of about 11 400 m³. Every 4 weeks, a PUF blank was collected by handling a clean PUF as a sample but not drawing air through it. More details regarding sample collection, preparation, and analysis are presented elsewhere (12, 21).

PUF plugs and filters were Soxhlet extracted using a 1:1 mixture of hexane and dichloromethane. After drying over anhydrous sodium sulfate and reducing the volume to 20 mL, half of the extract was archived. For this study, we were able to obtain a limited set of archived weekly PUF and GFF extracts representing approximately 2500 (Alert) and 3000 m³ (Dunai) air. Five samples were from Alert for the months June, July, and August 1993 and January and April 1994, and three samples were from Dunai for the months June, July, and August 1993. GFF extracts were analyzed for the July 1993 and January 1994 Alert samples and for the July 1993 sample from Dunai Island. All extracts were fortified with

TABLE 1. Sampling Information and Concentrations of Total PCNs and PCBs

sample	date	latitude/longitude (initial)	latitude/longitude (final)	air vol (m ³)	ΣPCN ^a (pg m ⁻³)	ΣPCB ^b (pg m ⁻³)
Barents Sea						
air1	96-07-18/19	71°8' N/21°35' E	73°34' N/24°60' E	945		
air2	96-07-19/21	73°34' N/25°1' E	73°47' N/25°40' E	1258	32.0	88.6
air3	96-07-21/22	73°52' N/25°60' E	78°25' N/56°10' E	659		
air4	96-07-22/23	77°5' N/41°15' E	78°25' N/56°10' E	710		
air5	96-07-23/24	78°25' N/56°60' E	80°18' N/65°43' E	623	48.7	163
				mean	40.4	126
Eastern Arctic Ocean						
air6	96-07-24/25	80°59' N/67°42' E	81°44' N/65°53' E	846		
air7	96-07-25/26	81°46' N/65°39' E	82°49' N/65°39' E	767		
air8	96-07-26/27	82°53' N/65°37' E	83°50' N/66°56' E	1096	12.7	15.5
air9	96-07-28/29	84°48' N/71°41' E	85°22' N/71°41' E	891		
air10	96-07-29/30	85°23' N/71°40' E	85°34' N/72°18' E	876		
air11	96-07-30/01	85°40' N/72°52' E	86°20' N/74°15' E	1221	16.0	22.1
air12	96-08-01/02	86°55' N/86°50' E	87°3' N/123°8' E	709		
air13	96-08-03/04	87°1' N/129°50' E	86°23' N/142°12' E	855	13.2	24.7
air14a	96-08-23	87°9' N/144°48' E	87°4' N/142°17' E	777		
air14b	96-08-23/24	87°4' N/142°17' E	86°29' N/130°6' E	771		
air14c	96-08-24/25	86°29' N/130°6' E	86°27' N/130°57' E	1168		
air14d	96-08-25/26	86°27' N/130°57' E	85°26' N/137°20' E	835	10.4	53.4
air15	96-08-29/30	85°24' N/152°17' E	85°31' N/155°3' E	1015		
air16	96-08-30/31	85°31' N/155°3' E	85°33' N/156°35' E	1232		
air17	96-08-31/01	85°33' N/156°37' E	85°40' N/160°22' E	669	14.8	27.1
air18	96-09-02/03	86°57' N/152°54' E	87°37' N/146°47' E	929		
air19	96-09-03/04	87°37' N/146°47' E	87°37' N/158°28' E	956		
air20	96-09-04/05	87°37' N/158°28' E	87°10' N/169°13' E	984	7.8	20.4
air21	96-09-07/08	88°36' N/179°38' E	88°52' N/179°58' E	768		
air22	96-09-08/09	88°59' N/179°59' E	89°54' N/156°9' E	930		
air23	96-09-10/12	89°51' N/51°11' E	87°60' N/23°19' E	1265	7.6	35.3
air24	96-09-12/13	87°60' N/23°19' E	86°30' N/19°33' E	1306		
air25	96-09-13/14	86°25' N/19°1' E	85°31' N/12°30' E	1030		
air26	96-09-14/15	85°31' N/12°30' E	85°33' N/10°55' E	873	9.2	12.9
air27	96-09-15/16	85°33' N/10°55' E	84°37' N/15°40' E	931		
air28	96-09-16/17	84°33' N/15°37' E	84°2' N/11°18' E	767		
air29	96-09-17/18	84°1' N/11°11' E	82°41' N/13°19' E	989	15.4	19.2
air30	96-09-21/22	78°15' N/15°39' E	74°37' N/14°34' E	883	8.5	12.8
				mean (SD)	11.6 (3.2)	24.3 (12.3)
Norwegian Sea						
air31	96-09-22/23	74°29' N/14°37' E	71°4' N/15°51' E	770		
air32	96-09-23/24	70°42' N/15°58' E	67°29' N/12°54' E	797		
air33	96-09-24/25	67°29' N/12°54' E	63°23' N/6°19' E	793	5.8	113.5
air34	96-09-25/26	63°23' N/6°18' E		680	8.3	82.8
				mean	7.1	75.1
Alert 1993–1994						
January PUF					2.5	57.3
April PUF					0.91	29.1
June PUF					8.0	9.9
July PUF					1.4	64.1
August PUF					3.7	27.8
July GFF					0.1	NA
January GFF					0.08	NA
				mean ^c (SD)	3.5 (2.7)	37.6 (22.5)
Dunai 1993						
June PUF					1.2	30.7
July PUF					0.31	32.2
August PUF					1.0	26.9
July GFF					NA	0.1
				mean ^c (SD)	0.84 (0.47)	29.9 (2.7)
Chicago 1995						
					68	350
Augsburg (Germany) 1992–1993 ^d						
				60	NR	

^a ΣPCN represent PUF values for combined eastern Arctic Ocean samples. ^b ΣPCB values for Alert and Dunai from Stern et al. (12); Chicago values from Harner and Bidleman (10, 19); approximately 25 PCB congeners were quantified in the Barents Sea and northeast Arctic Ocean samples. These same congeners in the Alert 1994 samples accounted for 45% of ΣPCB. Therefore, an adjustment factor of 2.22 (i.e., 1/0.045) was applied to ΣPCB for the Barents Sea and northeast Arctic Ocean samples (the adjusted values appear in this table). ^c Mean of PUF values. NA, not analyzed. NR, not reported. ^d Average of 9-month monitoring data from seven stations (9).

TABLE 2. Concentrations and TEQs for Dioxin-like PCBs and PCNs in Arctic and Urban Air

sample	concentration (fg m ⁻³)										Σ TEQs (fg TEQ m ⁻³)		
	PCN				1-ortho PCBs				0-ortho PCBs				
	CN-66/67	CN-69	CN-63	CN-73	-105	-118	-114	-156	-77	-126	PCNs	1-ortho	0-ortho
<i>Oden 1996</i>													
blank (mean)	4.6	39.3	18	5.9	0.7	12	0.6	1.0	0.6	0.6			
Barents Sea													
1,2	70	505	227	72	519	2073	28	111	133	3.9			
3,4,5	18	28*	11*	12*	994	7 571	129	311	561	6.1			
mean	44	267	119	42	757	4822	79	211	347	5.0	0.99	0.703	0.34
Eastern Arctic Ocean													
6,7,8	13	77	37	15	136	531	NQ	27	38.9	1.0			
9,10,11	37	228	112	40	137	576	NQ	32.8	32.2	1.9			
12,13	47	297	136	42	34.3	171	2.5	9.6	20.2	0.5*			
14a to 14d	11	41*	16*	12*	519	2749	46.5	64.0	261	3.0			
15,16,17	7*	28*	10*	12*	159	884	13.0	38.2	37.2	1.3			
18,19,20	50	310	140*	12*	40.9	195	NQ	8.9	14.8	1.0			
21,22,23	7*	65*	30*	12*	111	750	14.2	32.2	22.3	1.4			
24,25,26	15	78	38	12*	97.3	490	9.7	23.0	19.8	0.8			
27,28,29	52	321	147	51	59.4	306	NQ	10.1	14	0.3*			
30	7*	65*	30*	12*	NA	NA	NA	NA	NA	NA			
mean	24.7	151	67.2	21	144	739	17.2	27.3	51.1	1.3	0.548	0.111	0.151
Norwegian Sea													
31,32,33	7*	65*	30*	12*	NA	NA	NA	NA	NA	NA			
34	33	134	58	11	NA	NA	NA	NA	NA	NA			
mean	20	99.5	44	11.5							0.36		
<i>Alert 1993–1994</i>													
blank	0.03	0.3	0.1	<0.1	2				0.5	0.1			
January	1.2	1.4	0.6	ND	23.1				2.84	0.07*			
April	3.4	16.3	6.6	ND	31.3				3.1	0.07*			
June	5.4	43.6	20.3	ND	56.6				7.1	1.9			
July	22.3	33.5	21.4	ND	120				34.4	8.1			
August	NQ	2.9	1.9	ND	58.2				10.4	2.0			
mean	8.1	19.5	10.2	ND	57.8	260 ^b	50 ^b	50 ^b	11.6	2.4	0.076	0.082	0.25
<i>Dunai 1993</i>													
blank	0.04	0.5	0.1	<0.1	0.4				0.9	0.1			
June	0.61	2.3	1.5	ND	591				40.5	4.0			
July	0.03*	0.45	0.08*	ND	607				37.4	2.6			
August	0.01*	5.4	3.6	ND	372				17.8	0.9			
mean	0.22	2.7	1.7*	ND	523	1220 ^b	70 ^b	60 ^b	31.9	2.5	0.092	0.24	0.27
<i>Chicago 1995^c</i>													
mean (n = 15)	370	810	210	250	3270	8610	135	790	420	63	3.42	1.65	6.51

^a An asterisk (*) indicates samples below the LOD. Italicized values refer to samples which, when blank corrected, resulted in a negative; in these instances 2/3 of the LOD was inserted. ND, not detected (no quantifiable peak was observed). NA, not analyzed. NQ, ion ratios did not qualify. CN-66/67 (6–1) = 1,2,3,4,6,7/1,2,3,5,6,7; CN-69 (6–3) = 1,2,3,5,7,8; CN-63 (6–5) = 1,2,3,4,5,6; CN-73 (7–1) = 1,2,3,4,5,6,7. TEF values (PCNs) from Hanberg et al. (5): CN-66/67 = 0.002, CN-69 = 0.002, CN-63 = 0.002, CN-73 = 0.003. TEF values (PCBs) from Ahlborg et al. (25): PCB-77 = 0.0005, PCB-126 = 0.1, PCB-105 = 0.0001, PCB-114 = 0.0005, PCB-118 = 0.0001, PCB-156 = 0.0005. ^b Alert and Dunai PCB data for mono-ortho and Σ PCB taken from Stern et al. (12). ^c Chicago data from Harner and Bidleman (10).

¹³C₁₂-PCBs and analyzed by the same method described for the eastern Arctic samples.

Chicago. Air samples were collected in February–March 1995 on the roof of Farr Hall, a five-story building on the campus of the Illinois Institute of Technology, which is located just south of downtown Chicago and approximately 2 km inland from Lake Michigan. This work was part of a study to investigate concentrations and particle/gas partitioning of PCBs, PAHs, and PCNs in urban air. Sample volumes were approximately 400 m³. Details regarding sampling and analytical information are presented elsewhere (10, 19).

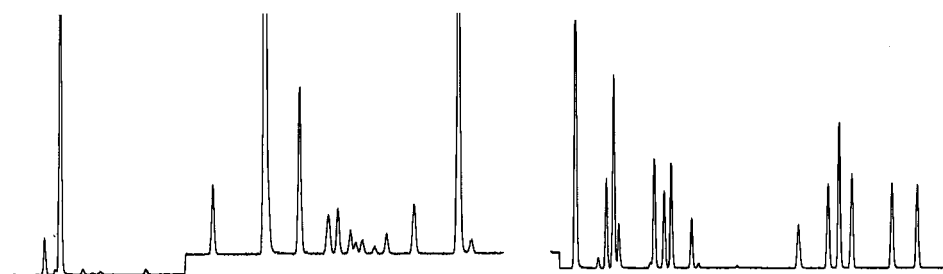
Results and Discussion

Quality Control. In the treatment of the shipboard samples, five of the second PUFs in the train were analyzed to assign blank levels. Limit of detection (LOD) values were calculated as mean blank + 3 SD. For compounds that had air concentrations near the LOD (this was sometimes the case

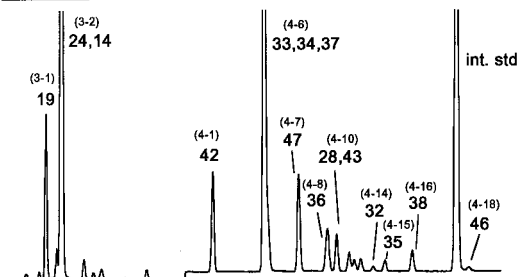
for the 6–7-Cl PCNs), a blank correction sometimes resulted in a negative value. In these instances two-thirds of the LOD was inserted and is italicized in Table 2. In GC–NIMS analysis, peaks had to meet two criteria to qualify. The first criteria was that the ion ratio (target ion:qualifier ion) had to be within $\pm 20\%$ of the value for the standard. Second, the sample peaks were required to exceed the LOD. For the Alert and Dunai samples quantified in this study, peaks qualified if they passed the ion ratio test and exceeded the single blank value. Analytes that passed these screening tests were blank corrected and adjusted using recovery factors.

Mean GC–NIMS recoveries of surrogate ¹³C₁₂-PCB in the eastern Arctic Ocean/Alert and Dunai samples were PCB 81, 72%/76%; PCB 77, 78%/79%; PCB 126, 80%/74%; and PCB 169, 95%/76%. Recoveries of unlabeled mono-ortho PCBs in fraction F1 were PCB 105, 98 \pm 9%; PCB 114, 70 \pm 6%; PCB 118, 78 \pm 6%; and PCB 156, 91 \pm 8%. Multi-ortho PCBs in the shipboard samples were determined in fraction F1 by

Halowax 1014



3/4-Cl PCNs Alert - June '93



5/6-Cl PCNs

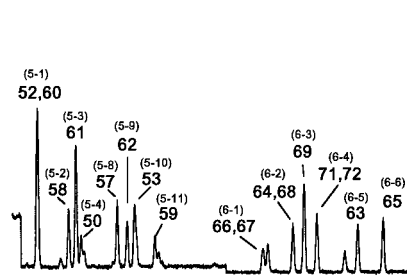


FIGURE 2. GC-NIMS chromatograms of technical PCN standard (Halowax 1014) and an air sample from Alert. The vertical scale of the 5/6-Cl section of the chromatogram in the Alert sample is magnified by a factor of 10. Peaks are labeled according to IUPAC numbers and by homologue group and elution order (in parentheses) (10).

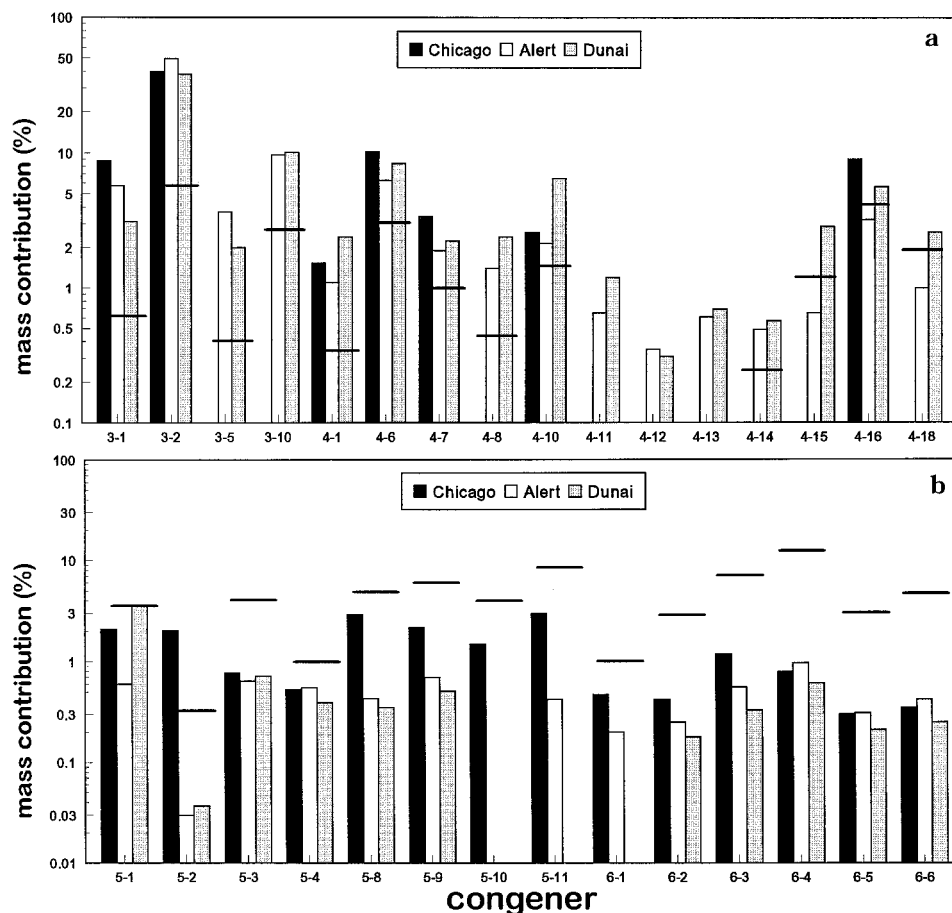


FIGURE 3. Mass distribution of PCN congeners at the sample locations. Solid bars represent mass contributions in Halowax 1014. Peaks are numbered by homologue group and elution order as presented in Harner and Bidleman (10).

GC-ECD against a standard of 56 congeners. Of these 56 congeners, approximately 25 were quantified, and recoveries

($n=4$) were $122 \pm 26\%$. Other congeners were not quantified because they were not present or were excluded due to

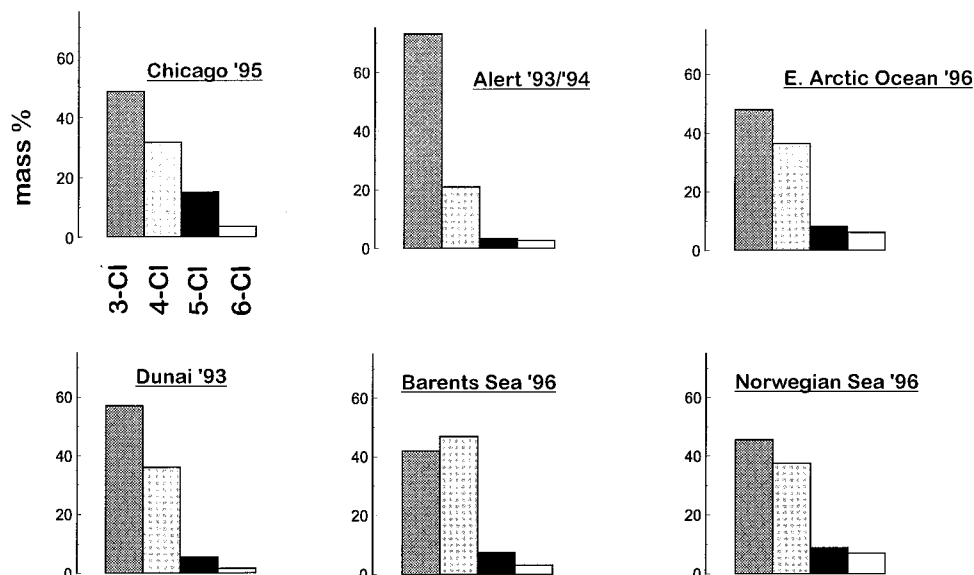


FIGURE 4. Homologue profiles for PCNs at the various sampling locations (see Figure 1).

problems with interfering peaks. LOD values (fg m^{-3}) for multi-ortho PCBs determined by GC-ECD were in the range <100 – 2900 . GC-NIMS LOD values for mono-/non-ortho congeners were lower: PCB 105, 2.0; PCB 114, <0.30 ; PCB 118, 19.2; PCB 156, 2.1; PCB 77, 1.5; PCB 81, 1.4; PCB 126, 0.3; and PCB 169, 0.40. For PCNs in F1-2, recoveries ranged from 35% for the volatile 3-Cl congeners to 95% for the higher molecular weight 6- and 7-Cl homologues. LOD values for individual PCN congeners in the eastern Arctic Ocean samples ranged from 3 to 680 fg m^{-3} .

PCNs in Air. Concentrations of ΣPCNs (pg m^{-3}) at each of the sampling sites are summarized in Table 1 and averaged 40 ($n = 2$) for the Barents Sea, 11.6 ± 3.2 ($n = 10$) for the eastern Arctic Ocean, and 7.1 ($n = 2$) for the Norwegian Sea. Values at the monitoring stations were Alert 3.5 ± 2.7 ($n = 5$) and Dunai Island 0.84 ± 0.47 ($n = 3$) (pg m^{-3}). Except for the Barents Sea samples, these are approximately an order of magnitude lower than levels reported in urban areas. The average concentration of PCNs in Chicago during the winter (February–March 1995) was 68 pg m^{-3} (10), and the yearly average for Augsburg, Germany (1992–1993) was 60 pg m^{-3} (9).

Figure 2 shows GC-NIMS chromatograms for Halowax 1014 and a PUF sample from Alert. The PCN pattern in the sample and standard are well matched, with the sample showing significant enrichment of the lower molecular weight congeners and depletion of the higher molecular weight congeners relative to Halowax 1014. This is further demonstrated in Figure 3, which compares congener mass profiles for the land-based Arctic Ocean sites and the Chicago samples with mass contributions in Halowax 1014. The Arctic Ocean and Chicago samples exhibit a greater proportion of the less chlorinated congeners as compared to the standard. This fractionation is also suggested by Figure 4, which shows the average homologue mass distribution at the sampling sites. The 3-Cl and 4-Cl congeners account for approximately 80% of the total mass in Chicago and are enriched to 90–95% of the total mass in the arctic samples. This may be due to preferential volatilization of the lighter PCN congeners (i.e., global fractionation; 22). An alternate explanation may involve differences in source signatures. Halowax 1001 and 1099 accounted for 65% of the market share of Halowax sales (6) and are dominated by 3-Cl (40%) and 4-Cl (40%) congeners. Their contribution in Halowax 1014 is smaller: 3-Cl (14%) and 4-Cl (34%) (10).

Before any definitive statements can be made regarding PCN transport and global distribution, more studies are

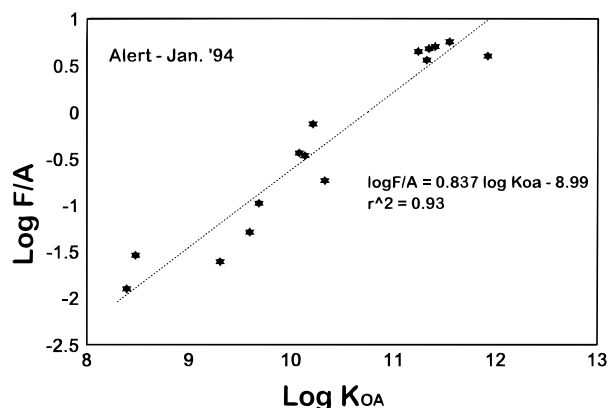


FIGURE 5. Particle/gas partitioning of PCNs in a sample from Alert collected in January 1994. F and A represent particle-phase and gas-phase concentrations (pg m^{-3}).

required to investigate PCN partitioning in the atmosphere as well as other environmental media. A good starting point is to look at the particle/gas partitioning of PCNs in air, which is important in the transport of chemicals from sources to remote areas as well as in their deposition from the atmosphere to ecosystems. Absorption of chemicals to particles can be described using the octanol–air partition coefficient, K_{OA} (19, 23), which has been recently measured for PCN congeners as a function of temperature (24). Figure 5 is a log–log plot of the filter/adsorbent (F/A) ratio versus K_{OA} for a January 1994 air sample from Alert. F and A represent the particle-phase and gas-phase concentrations (pg m^{-3} air).

PCBs in Air. Concentrations of total PCBs (approximately 100 congeners) were taken from Stern et al. (12) and are summarized in Table 1 for the five samples from Alert and three samples from Dunai. Average ΣPCB (pg m^{-3}) were 38 ± 23 and 30 ± 3 , respectively. For the Barents Sea and northeast Arctic Ocean samples, ΣPCB (Table 1) were determined by combining the GC-ECD results for fraction F1-1 (mostly multi-ortho congeners) and the GC-NIMS results for fraction F1 (mono-ortho) and F1-2 (non-ortho PCBs).

When compared to values of ΣPCB reported for the warm months (May–August) at Alert (38 pg m^{-3}) in 1994, levels in the Barents Sea (126 pg m^{-3}) and Norwegian Sea (75 pg m^{-3}) were 2.5–3.5 times greater, while levels in the east Arctic

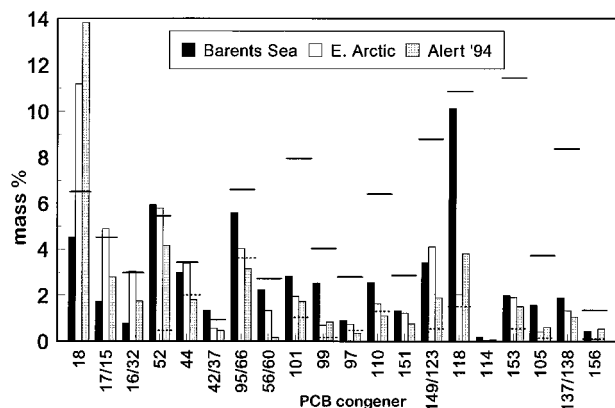


FIGURE 6. Mass percent contributions of PCB congeners in arctic air samples. Solid and dashed bars represent upper and lower mass percentages in technical formulations (i.e., Aroclor 1242 and 1254, Clophen A50, and A60) (25).

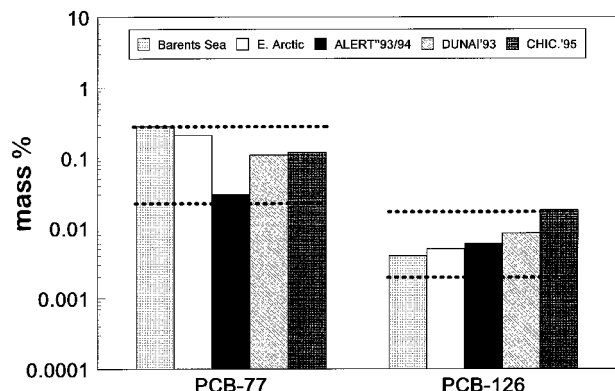


FIGURE 7. Mass distribution for coplanar PCBs at the sample locations. Dashed lines represent upper and lower mass contributions in technical PCB formulations (8, 16).

Ocean were in good agreement (37 pg m^{-3}). It should be noted that ΣPCBs for the shipboard samples were adjusted using a factor of 2.2 (as explained in Table 1) to account for the fact that only 25 congeners were quantified as compared to 86 by Stern et al. (12). Levels of ΣPCB were approximately 4–10 times greater than ΣPCN in arctic samples (except at Dunai where ΣPCB was ~ 30 times greater) and 5–6 greater in Chicago samples (19) (Table 1). Mass percent contributions of individual PCB congeners are summarized in Figure 6 for the Barents Sea, eastern Arctic Ocean, and Alert 1994 samples. In almost all cases, the results are within the ranges reported for technical PCB mixtures (25). The northeast Arctic Ocean profile is similar to Alert 1994 and is dominated by the lower molecular weight 3- and 4-Cl congeners. The Barents Sea sample exhibits a profile enriched in the higher molecular weight congeners, especially PCB 118. Schultz et al. (25) found that the PCB 118 content of Clophen A50 was quite high (10.9%) as compared to the percentage (6.4%) in the approximate equivalent U.S. mixture, Aroclor 1254. A previous study (12) also found enrichment in the 5-Cl and 6-Cl at the Dunai site during the summer months.

Concentrations of coplanar PCB congeners, 77 and 126, in arctic air are summarized in Table 2. Values for congeners 81 and 169 were excluded since most samples were near or below the detection limits, and ion ratios were not satisfactory. The mass percentage contributions of congeners 77 and 126 have been reported in Aroclor mixtures 1242 and 1254 (16) and Clophen mixtures (8). Figure 7 shows that in all cases their mass contribution in arctic air samples is within the range reported for technical mixtures. Average concentrations (fg m^{-3}) of congeners 77 and 126 in the Barents Sea

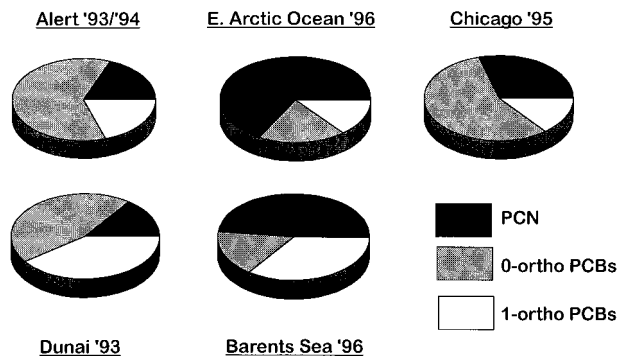


FIGURE 8. Percent TCDD TEQ contributions of PCNs, coplanar PCBs (congeners 77 and 126), and mono-ortho (congeners 105, 114, 118, and 156) in air samples from arctic and urban air.

were 347 and 5.0, respectively, with lower values observed at the other locations: eastern Arctic Ocean, 51.1 and 1.3; Alert, 11.6 and 2.4; Dunai, 31.9 and 2.5. The only other reported values are those of Schlabach et al. (15), who measured coplanar PCBs and polychlorinated dioxins/furans (PCDD/PCDF) in two samples collected at Zeppelin Mountain in spring/summer 1995, about 2 km south of Ny-Ålesund, Spitsbergen. Here the average values for congeners 77 and 126 were 193 and 0.73 fg m^{-3} , respectively, which is within the range of values reported for *Oden* samples (Table 2). However, the relative proportion of 77/126 was high for Ny-Ålesund (~ 264) as compared to values reported in this study—69 (Barents Sea), 39 (northeast Arctic Ocean), 4.8 (Alert), 12.8 (Dunai), and 6.7 (Chicago).

Implications Regarding Toxicity. Because of their shape and size, some coplanar PCBs, mono-ortho PCBs (and a few di-ortho congeners), and PCNs exhibit 2,3,7,8-tetrachlorodibenzodioxin (TCDD) toxicity. Toxic equivalent factors (TEFs) have been determined for PCBs (25) and several 6–7 chlorinated PCN congeners (5). By calculating TCDD toxic equivalents (TEQs), it is possible to compare dioxin-like toxicity of different compounds on a common scale. TEQs are calculated by multiplying the air concentration of the particular compound by its TEF value. A recent study has shown that approximately 14% of the TCDD toxicity measured in plasma in an Inuit population from Nunavik (arctic Quebec) could be attributed to non-ortho PCBs. This contribution was slightly higher (20%) in southern Quebec (27).

Table 2 and Figure 8 summarize the air concentrations and TEQ values for non- and mono-ortho PCBs and several dioxin-like PCNs at the sample locations. In most cases, the highest TEQ contribution is attributed to the coplanar PCBs, mostly congener 126 (Table 2). The Dunai and Barents Sea samples have high concentrations and elevated TEQ contributions of the mono-ortho congeners, mostly congeners 118 and 105. The PCNs also make an important contribution—accounting for 13–67% of the TEQ at the arctic sites and $\sim 30\%$ in Chicago. At Ny-Ålesund, the ΣTEQ (fg TEQ m^{-3}) was on average ($n = 2$) 0.019 for the coplanar PCBs and 1.7 for the PCDD/PCDF (15). In this study, ΣTEQ (PCNs + mono-/non-ortho PCBs) were 2.0 (Barents Sea), 0.81 (eastern Arctic Ocean), ≥ 0.36 (Norwegian Sea), 0.41 (Alert), 0.60 (Dunai), and 11.6 (Chicago).

Source Attribution Using Five-Day Back-Trajectories. To relate episodes of high concentration (Table 1) to source regions, three-dimensional 5-day air parcel back-trajectories arriving at the sampling location at a pressure level of 850 and 925 hPa (i.e., ~ 1.5 and 0.75 km altitude) were determined for all 34 individual air samples (14 combined samples). Trajectories (obtained from the Atmospheric Environment Service) were determined every 6 h, resulting in eight

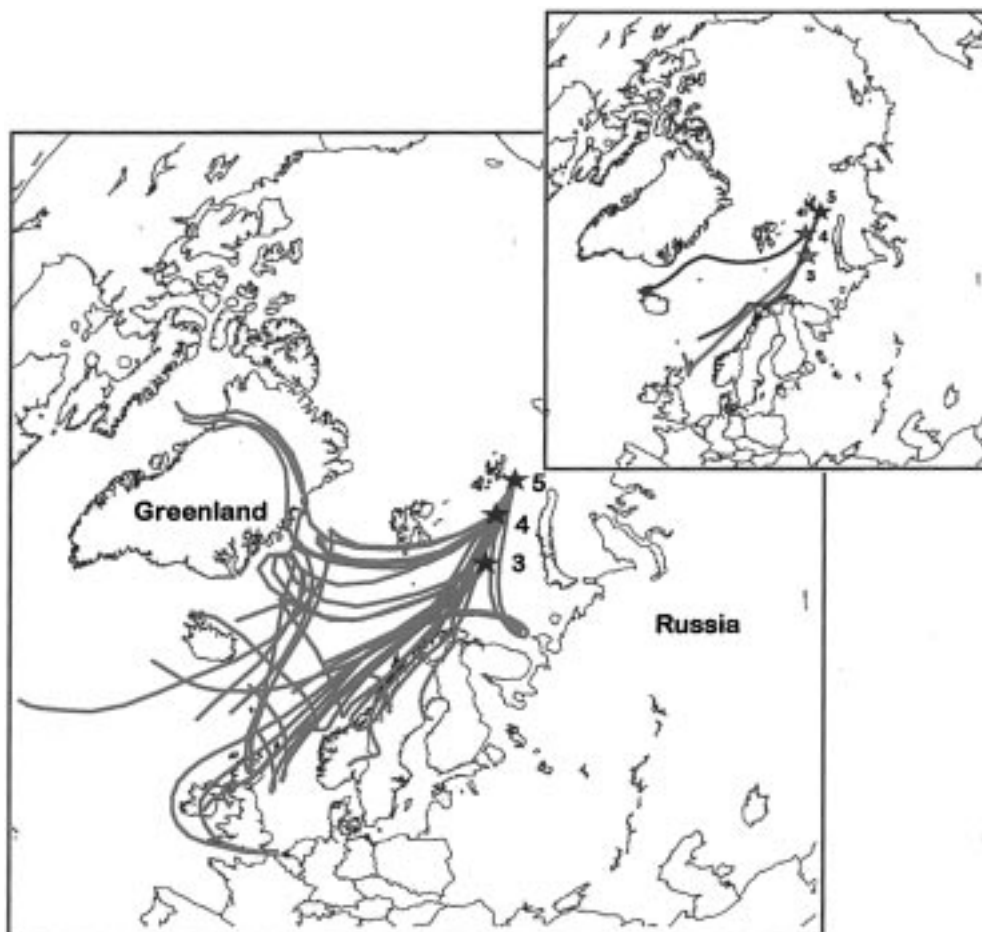


FIGURE 9. Three-dimensional 5-day air parcel back-trajectories arriving at the ship at 850 and 925 hPa for a combined sample with elevated $\Sigma\text{PCN} + \Sigma\text{PCB}$ levels. Inset figure in top right corner shows the average trajectory for each station.

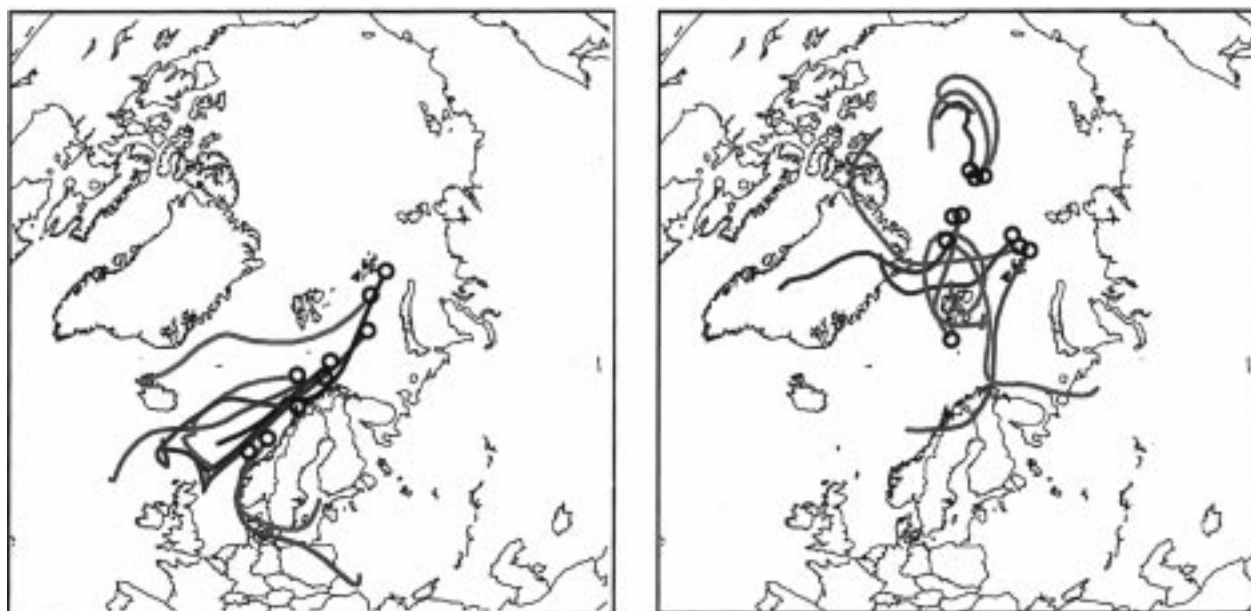


FIGURE 10. Average back-trajectories (850 and 925 hPa) for four combined samples having the highest concentration of ΣPCB (left figure) and for four samples with the lowest concentrations (right figure). Open circles represent sample stations.

trajectories for a 24-h sample (i.e., four trajectories at two pressure levels).

Trajectories (850 and 925 hPa) for the combined sample (stations 3–5) that exhibited elevated PCBs and PCNs are shown in Figure 9. The inset figure shows the daily average

trajectory for each location. Air parcels arriving at stations 3–5 spent much of their 5-day history near coastal Norway, the United Kingdom, and the North Sea, implicating these regions as potential sources. Further evidence of a European source is demonstrated in Figure 10, which shows the average

5-day back-trajectories for the four samples having the highest Σ PCB concentrations (1+2; 3+4+5; 31+32+33; 34) (samples 1+2 and 3+4+5 also had the highest Σ PCN) as compared to the four samples having the lowest concentrations (6+7+8; 18+19+20; 24+25+26; 30). Trajectories for the elevated samples stem back in a southerly direction toward Europe. For the low-concentration samples, air parcels spent most of their 5-day history over the Arctic Ocean; although a few pass over land but in non-industrial regions (e.g., Greenland, Canadian Archipelago, northern Scandinavia).

It should be noted that errors of approximately 20% of the distance traveled are typical for these sorts of trajectories (28). Added to this is the uncertainty associated with a moving ship, which we assumed to be stationary to simplify the trajectory analysis. With this scale of uncertainty, it is difficult to attribute episodes of high PCB or PCN concentrations to specific sources (e.g., countries).

In conclusion, PCNs and PCBs have been quantified for the first time in arctic air samples. Five-day back trajectories suggest that high concentrations of PCBs and PCNs for shipboard samples collected in the Barents Sea, eastern Arctic Ocean, and Norwegian Sea are related to a continental/European source region. The relative dioxin-type toxicity contribution (TEQ) of PCBs and PCNs indicates that PCNs account for 13–67% of the relative TEQ in arctic air as compared to 30% in urban Chicago (10, 19). More work is merited to investigate concentrations of coplanar PCBs and PCNs in arctic samples, since these compounds may elicit significant human and animal toxicities.

Acknowledgments

We thank the Swedish Polar Research Secretariat, Swedish Environmental Protection Agency, Natural Sciences Research Council, Knut and Alice Wallenberg Foundation, the crew of *Oden* for their support in the eastern Arctic Ocean expedition, and Eva Jakobsson and Åke Bergman (Stockholm University) for their gifts of PCN congeners. Funding was provided by the Northern Contaminants Program, Canadian Department of Indian Affairs and Northern Development.

Literature Cited

- Järnberg, U.; Asplund, L.; de Wit, C.; Grafström, A.-K.; Haglund, P.; Jansson, B.; Lexén, K.; Strandell, M.; Olsson, M.; Jonsson, B. *Environ. Sci. Technol.* **1993**, *27*, 1364–1374.
- Falandysz, J.; Rappe, C. *Environ. Sci. Technol.* **1996**, *30*, 3362–3370.
- Koistinen, J.; Paasivirta, J.; Vuorinen, P. J. *Chemosphere* **1989**, *19*, 527–530.
- Asplund, L.; Jansson, B.; de Wit, C.; Bergek, S.; Hjelt, M.; Rappe, C.; Odsjö, T.; Olsson, M. 10th International Conference on Organochlorine Compounds, Dioxin '90, Bayreuth, Germany, September 10–14, 1990; Extended Abstract.
- Hanberg, A.; Wern, F.; Asplund, L.; Haglund, P.; Safe, S. *Chemosphere* **1990**, *20*, 1161–1164.
- Crookes, M. J.; Howe, P. D. *Environmental hazard assessment: halogenated naphthalenes*, Report TSD/13; Department of the Environment: London, 1993.
- Oehme M.; Manø, S.; Mikalsen, A. *Chemosphere* **1987**, *16*, 143–153.
- Haglund, P.; Asplund, L.; Järnberg, U.; Jansson, B. *J. Chromatogr.* **1990**, *507*, 389–398.
- Dörr, G.; Hippelein, M.; Hutzinger, O. *Chemosphere* **1996**, *33*, 1563–1568.
- Harner, T.; Bidleman, T. F. *Atmos. Environ.* **1997**, *31*, 4009–4016.
- Järnberg, U.; Asplund, L.; de Wit, C.; Egeback, A.-L.; Wideqvist, U.; Jakobsson, E. *Arch. Environ. Contam. Toxicol.* **1997**, *32*, 232–245.
- Stern, G. A.; Halsall, C. J.; Barrie, L. A.; Muir, D. C. G.; Fellin, P.; Rosenberg, B.; Rovinski, F.; Kononov, E.; Postoukov, B. *Environ. Sci. Technol.* **1997**, *31*, 3619–3628.
- Weis, I. M.; Muir, D. C. G. *Environ. Pollut.* **1997**, *96*, 321–333.
- Muir, D. C. G.; Norstrom, R. J.; Simon, M. *Environ. Sci. Technol.* **1988**, *22*, 1071–1079.
- Schlabach, M.; Biseth, A.; Gunderson, H. 16th International Symposium on Chlorinated Dioxins and Related Compounds, Dioxin '96, Amsterdam, The Netherlands, August 12–16, 1996; Extended Abstract.
- Schwartz, T. R.; Tillit, D. E.; Feltz, K. P.; Peterman, P. H. *Chemosphere* **1993**, *26*, 1443–1460.
- Billings, W. N.; Bidleman, T. F. *Environ. Sci. Technol.* **1980**, *14*, 679–683.
- Halsall, C. J.; Barrie, L. A.; Fellin, P.; Muir, D. C. G.; Billeck, B. N.; Lockhart, L.; Rovinsky, F. Ya.; Kononov, E. Ya.; Pastukhov, B. *Environ. Sci. Technol.* **1997**, *31*, 3593–3599.
- Harner, T.; Bidleman, T. F. *Environ. Sci. Technol.* **1998**, *32*, 1494–1502.
- Falconer, R. L.; Bidleman, T. F.; Cotham, W. E. *Environ. Sci. Technol.* **1995**, *29*, 1666–1673.
- Fellin, P.; Barrie, L. A.; Daugherty, D.; Toom, D.; Grift, N.; Lockhart, L.; Billeck, B. *Sci. Total Environ.* **1996**, *15*, 2380–2386.
- Wania, F.; Mackay, D. *Environ. Sci. Technol.* **1996**, *30*, 390A–396A.
- Finizio, A.; Mackay, D.; Bidleman, T. F.; Harner, T. *Atmos. Environ.* **1997**, *31*, 2289–2296.
- Harner, T.; Bidleman, T. F. *J. Chem. Eng. Data* **1998**, *43*, 40–46.
- Schultz, D. E.; Petrick, G.; Duinker, J. *Environ. Sci. Technol.* **1989**, *23*, 852–859.
- Ahlborg, U. G.; Becking, G. C.; Birnbaum, L. S.; Brouwer, A.; Derks, H. J. G. M.; Feeley, M.; Golor, G.; Hanberg, A.; Larsen, J. C.; Liem, A. K. D.; Safe, S.; Schlatter, C.; Waern, F.; Younes, M.; Yrjanheikki, E. *Chemosphere* **1994**, *28*, 1049–1067.
- Ayotte, P.; Dewailly, E.; Ryan, J. J.; Bruneau, S.; Lebel, G. *Chemosphere* **1997**, *34*, 1459–1468.
- Stohl, A. *Atmos. Environ.* **1998**, *32*, 947–966.

Received for review March 27, 1998. Revised manuscript received June 23, 1998. Accepted July 7, 1998.

ES9803106