

Air–Water Gas Exchange of Organochlorine Compounds in Lake Baikal, Russia

LAURA L. MCCONNELL,^{*,†}
JOHN R. KUCKLICK,[‡]
TERRY F. BIDDLEMAN,^{§,△}
GENADI P. IVANOV,^{||} AND
SERGEY M. CHERNYAK[⊥]

United States Department of Agriculture, Agricultural Research Service, Environmental Chemistry Laboratory, Beltsville, Maryland 20705, National Marine Fisheries Service, South East Fisheries Science Center, Charleston, South Carolina 29422-2607, Department of Chemistry and Biochemistry and Marine Science Program, University of South Carolina, Columbia, South Carolina 29208, Russian Academy of Science, Limnological Institute, Irkutsk, Russia, and Institute of Fisheries, Moscow, Russia

Air and surface water samples were collected at Lake Baikal, Russia, during June 1991 to determine concentrations of organochlorine pesticides and polychlorinated biphenyl (PCB) congeners. These data were combined with Henry's law constants to estimate the gas flux rate across the air–water interface of each compound class. Air samples were collected at Lake Baikal and from nearby Irkutsk. Water samples were collected from three mid-lake stations and at the mouth of two major tributaries. Average air concentrations of chlorinated bornanes (14 pg m^{-3}), chlordanes (4.9 pg m^{-3}), and hexachlorobenzene (HCB) (194 pg m^{-3}) were similar to global background or Arctic levels. However, air concentrations of hexachlorocyclohexanes (HCHs), DDTs, and PCBs were closer to those observed in the Great Lakes region. Significantly higher levels of these three compound classes in air over Irkutsk suggests that regional atmospheric transport and deposition may be an important source of these persistent compounds to Lake Baikal. Air–water gas exchange calculations resulted in net depositional flux values for α -HCH, γ -HCH, DDTs, and chlorinated bornanes at 112, 23, 3.6, and $2.4 \text{ ng m}^{-2} \text{ d}^{-1}$, respectively. The total net flux of 22 PCB congeners, chlordanes, and HCB was from water to air (volatilization) at 47, 1.8, and $32 \text{ ng m}^{-2} \text{ d}^{-1}$, respectively.

Introduction

Within the former Soviet Union, total pesticide usage was approximately 100 000 t in 1965 and 160 000 t in 1970 (1). In 1987, the Academy of Agriculture officials in the Soviet Union predicted that pesticide usage in 1990 would be 480 000 t (2). Following drastic changes within the economic system in Russia, however, this estimate may or may

not be accurate. As in the United States, organochlorine insecticides were heavily used in the Soviet Union during the 1960s and 1970s, but increasingly these chemicals were replaced by less persistent pesticides such as organophosphorus products. However, organochlorine pesticides as well as polychlorinated biphenyls (PCBs) are extremely persistent in the environment and have a tendency to bioaccumulate in animals, causing toxic effects. Lake Baikal is the world's deepest freshwater lake (1741 m at its deepest point) and is 20–25 million years old. Its basin holds approximately 20% of the world's unfrozen freshwater (23 000 km^3), and it is home to over 1500 endemic species of plants and animals (3). The long residence time ($t_R \approx 350 \text{ yr}$) and cold temperature of water in Lake Baikal make it especially vulnerable to the buildup of persistent organic pollutants (7).

Population within the lake's basin is relatively sparse; however, there are major industrial centers, Irkutsk [population = 640 500 (4)], Ulan-Ude, Angarsk, Shelekhov, and Baikalsk, located within 0–100 km of the lake (Figure 1). Lake Baikal is located in a mountainous area, and runoff from these mountains feeds 200–300 tributaries that flow into the lake. The largest river entering the lake is the Selenga, which flows north through the city of Ulan-Ude. It is believed that the Selenga River is a major source of pollutants to the lake (5, 6). The only out-flowing river is the Angara, which flows northwest to meet the Yenisey River. As with other large water bodies, i.e., the Great Lakes (8), atmospheric deposition is probably an important pathway for organic pollutants to enter the lake. In order to investigate atmospheric inputs of organochlorine pollutants, concentrations of polychlorinated biphenyls (PCBs), chlorinated bornanes (CHBs, e.g., toxaphene), DDTs, chlordanes, hexachlorocyclohexanes (HCHs), and hexachlorobenzene (HCB) were determined simultaneously in the air and surface water of Lake Baikal. Estimates of the gas flux and loadings of organochlorine pesticides and PCBs across the air–water interface and estimates of net atmospheric loadings were calculated. Airborne organochlorine pesticides and PCBs were also determined in the nearby city of Irkutsk to investigate local sources of these compounds.

Experimental Method

Sample Collection. Air samples were collected using a glass fiber filter–polyurethane foam system. An initial screening of glass fiber filter extracts showed no measurable concentrations of target analytes. Results presented are from the gas-phase only. Water was processed by passing through a glass fiber filter followed by a C_8 -bonded silica cartridge (low-volume samples) or an XAD-2 resin column (high-volume samples). Details of sample collection,

* Corresponding author telephone: (301)504-6298; fax: (301)504-5048; e-mail address: mconnel@asrr.arsusda.gov.

† U.S. Department of Agriculture.

‡ National Marine Fisheries Service.

§ University of South Carolina.

△ Present address: Atmospheric Environment Service, Downsview, Ontario M3H 5T4, Canada.

|| Russian Academy of Science.

⊥ Institute of Fisheries.

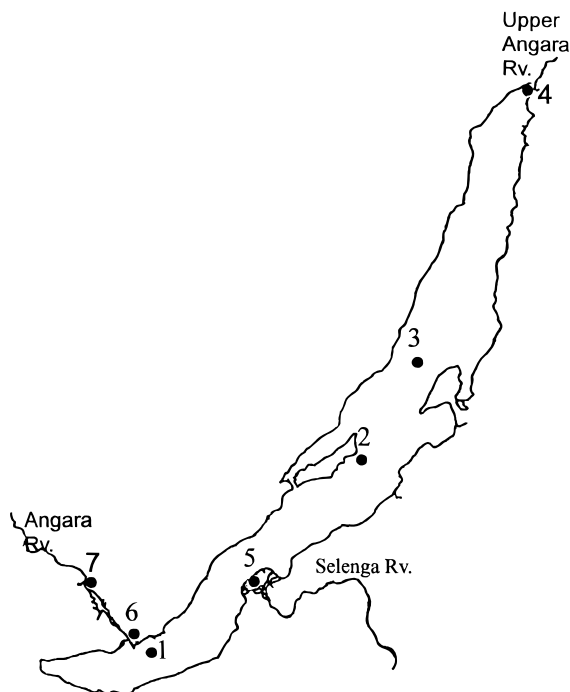


FIGURE 1. Lake Baikal, Russia: length, 625 km; surface area, 31 500 km²; maximum depth, 1741 m. Collection sites for air and water samples: 1, southern basin, depth = 1000 m; 2, central basin, depth = 1600 m; 3, northern basin depth = 900 m; 4, Upper Angara River; 5, Selenga River; 6, Lystvianka Hydromet station; 7, Irkutsk.

sorbent preparation, extraction, and cleanup procedures are given elsewhere (9–11).

Table 1 lists the date, site, volume, and temperature conditions for each air and water sample excluding the high-volume water samples, which are given elsewhere (10). Collection sites are illustrated in Figure 1. A total of 19 air samples were collected at three sites: the bow of the R/V *Vereshchagin*, a meteorological monitoring station (Hydromet) at Lystvianka on the lake shore, and the roof of the Limnological Institute in Irkutsk. Four samples were collected on board the R/V *Vereshchagin* (BKA1–4) from June 6 to June 11, and these were restricted to <426 m³ to reduce breakthrough of α -HCH and HCB to the second foam plug. Eleven air samples (BKA5–16) were taken at the Hydromet station from June 6 to June 28. Five of the samples from Hydromet (BKA5–7, BKA11–12, and BKA16) were ultra-high-volume (2211–3382 m³) in order to ensure detection of chlordanes, DDT, and CHBs, and the remainder were similar in volume to those collected on board ship. Three samples were obtained in Irkutsk from June 19 to June 24 (BKA17–19), and volumes were slightly larger than those from the ship (709–1394 m³) (17). Air temperatures ranged from 3.2 °C on June 15 to 22 °C on June 23. Wind speeds were generally calm at 1–5 m s^{−1} with the highest observed wind speed of 10 m s^{−1}.

High-volume (180 L), and low-volume (4 L), and surface water samples (depth 3–5 m) were collected during June 6–10, 1991, from the R/V *G. Yu. Vereshchagin* and during several 1-day trips from June 15 to June 25 from a smaller vessel (10). The majority of water samples were collected in the southern basin station 1 (BK2–6). One high-volume and one low-volume sample (BK7) were obtained from station 2 in the central basin, and one high-volume sample was obtained from station 3 in the northern basin. One low-volume sample was collected from the mouth of the Upper Angara river (BK1), and three low-volume samples

TABLE 1

Collection Data for Water and Air Samples^a

sample name	date	site	vol	temp (°C)
BK1	6/8	4	2.70 L	2.5
BK2	6/6	1	3.96 L	4.5
BK3	6/6	1	3.82 L	3.6
BK4	6/6	1	4.15 L	4.2
BK5	6/6	1	3.97 L	4.0
BK6	6/6	1	4.09 L	4.1
BK7	6/7	2	3.94 L	3.0
BK8	6/15	5	4.00 L	18
BK9	6/15	5	4.00 L	17.5
BK10	6/15	5	4.00 L	17
BKA1	6/6–7	1–2	310 m ³	5–16
BKA2	6/7–8	2–3	385 m ³	5.4–13
BKA3	6/8–9	3–2	277 m ³	5.4–12.0
BKA4	6/10–11	2–1	426 m ³	8.0–8.5
BKA5	6/6–9	6	2211 m ³	5.7–19.7
BKA6	6/9–12	6	2226 m ³	7.7–15.5
BKA7	6/12–15	6	2281 m ³	3.5–20.3
BKA8	6/15	6	283 m ³	7.9–8.8
BKA9	6/15–16	6	374 m ³	3.2–6.7
BKA10	6/16	6	404 m ³	5.5–11.6
BKA11	6/16–21	6	3382 m ³	3.9–21.6
BKA12	6/21–22	6	2168 m ³	10–15.6
BKA13	6/22–23	6	805 m ³	8.6–17.8
BKA14	6/23	6	310 m ³	8.6–22.2
BKA15	6/25	6	303 m ³	9.6–11.8
BKA16	6/25–28	6	1934 m ³	5.1–14.3
BKA17	6/19–20	7	709 m ³	NA ^b
BKA18	6/21–23	7	1394 m ³	NA
BKA19	6/23–24	7	867 m ³	NA

^a BK1–10 are low-volume water samples; BKA1–19 are high-volume air samples; data for high-volume water samples are given elsewhere (10). ^b NA, not available.

were collected from the mouth of the Selenga River (BK8–10). Surface water temperature was measured at each station and was 2.5 °C at the Upper Angara River mouth, 17–18 °C at the mouth of the Selenga River, and 3.0–4.5 °C in the open lake.

Analysis and Quality Control Methods. Low-volume water samples were only analyzed for HCHs. High-volume water and air samples were analyzed for all organochlorines and PCBs. Analysis was carried out by capillary gas chromatography (GC) on a 30-m DB-5 bonded phase column (J&W Scientific) using a Varian 3700 chromatograph with a ⁶³Ni electron capture detector (GC-ECD). GC conditions were as follows: injector temperature, 240 °C; detector temperature, 320 °C; carrier gas, H₂ at 30–40 cm s^{−1}; oven program: splitless injection at 90 °C (1 min hold), open split after 30 s, program at 6 °C/min to 260 °C. Chromatographic data were collected in the peak area mode using a Hewlett-Packard 3390 or Shimadzu Chromatopac CR3A integrator. OCs and toxaphene (CHBs) were also determined using capillary GC negative ion mass spectrometry (GC-NIMS) using a method published previously (10, 13).

HCHs were quantified against two external standards of concentrations slightly below and above those of the samples. PCBs and other organochlorines were quantified versus single-concentration standards using a mirex internal standard added just before injection. Samples were analyzed for 41 PCB congeners using Aroclors 1242 and 1254 as standards and percent composition information from ref 14 and 15.

Limits of detection and spike recovery data for the high-volume water samples, including all organochlorine pes-

ticides and PCBs, have been published earlier (10). Limits of detection were defined as the mean blank value plus three times the standard deviation of the blank. Three system blanks for HCHs were done on board ship by spiking approximately 100 mL of double distilled laboratory water transported from South Carolina with a δ -HCH surrogate solution, pretreating the cartridge with 5 mL of methanol and distilled water and pulling the spiked distilled water through the Teflon-tubing, GFF, and cartridge. The resulting blank \pm standard deviation (sd) values are 0.017 ± 0.006 ng and 0.11 ± 0.016 ng for α - and γ -HCH, respectively. The analytical limits of detection, therefore, are 0.035 ng for α -HCH and 0.16 ng for γ -HCH. At a water volume of 4 L, the limit of detection in surface water would be 0.009 ng L⁻¹ and 0.04 ng L⁻¹ for α - and γ -HCH, respectively.

α -, γ -, and δ -HCH standards were spiked into three samples at concentrations well above expected ambient levels. Absolute recovery results were 78 ± 4 , 71 ± 4 , and 73 ± 10 for α -, γ -, and δ -HCH, respectively. Relative recoveries were α -HCH/ δ -HCH = 1.1 and γ -HCH/ δ -HCH = 0.97. Recovery of δ -HCH was not significantly different from α - and γ -HCH ($p \leq 0.05$). Dissolved-phase (C_d) HCH concentrations in each sample were corrected using the mean blank and fractional recovery (R) of δ -HCH as specified elsewhere (9). High-volume water sample concentrations were also corrected using mean blank and fractional spike recovery values as described earlier (10).

Analytical blank foam plug values ranged from 41 pg for α -HCH to 570 pg for 4,4'-DDT for pesticides and from 50 pg for congener 180 to 2300 pg for congener 8 for polychlorinated biphenyls. At an average air volume of 300 m³ for the HCHs and 2000 m³ for the other organochlorines, the limits of detection (LOD = mean bulk \pm 3 SD) (pg m⁻³) in air were as follows: α -HCH, 0.23; γ -HCH, 2.3; *trans*-chlordane (TC), 0.79; *cis*-chlordane (CC), 0.90; *trans*-nonachlor (TN), 0.46; 4,4'-DDE, 0.70; 4,4'-DDT, 1.1; PCB congener 180, 0.045; PCB congener 87, 1.2. A detailed list of polyurethane foam blanks and limits of detection for organochlorines and Σ PCBs are given elsewhere (12). Foam plugs were spiked with a mixed organochlorine pesticide standard while in Baikal and were returned with the samples to check for losses during transport. Spike yields were 53% for HCB, 74–75% for the HCHs, and 88–113% for the other organochlorines (12). Gas-phase concentrations of organochlorines were corrected for mean blank and fractional spike values. Recovery values of 100% were assumed for DDTs, chlordanes, and nonachlors since experimental values were 104–113%. Spiking experiments with PCBs on foam plugs were not done, and concentrations were corrected using mean blanks only.

Concentration Data

Hexachlorocyclohexanes. In 1974, the approved formulation of HCH in the Soviet Union contained 90% γ -HCH (lindane); however, usage of the technical mixture was not completely banned. Also, γ -HCH was used in several formulations in combination other chemicals such as ethyl mercury chloride (mercuran), hexachlorobenzene (hexagamma), copper 2,4,5-trichlorophenolate (phentioran), and tetramethyl thiuram disulfide. Usually these formulations contained 10–50% γ -HCH (1). Also, as of 1974, γ -HCH was used together with DDT to control Colorado beetles on potatoes and some other insects. Methoxychlor, a DDT analog, was also added in some cases to the HCH/DDT formulation (1). In 1987, a formulation of 2–16% γ -HCH

TABLE 2

Concentrations of Hexachlorocyclohexanes and Hexachlorobenzene in Air and Water Samples^a

sample	α -HCH	γ -HCH	HCB
Vereshchagin			
BKA1	365	36	233
BKA2	341	63	138
BKA3	377	107	180
BKA4	377	99	251
Hydromet Station			
BKA7	643	112	NA ^b
BKA8	176	42	144
BKA9	294	56	156
BKA10	200	42	163
BKA13	456	120	NA
BKA14	1054	250	250
BKA15	683	183	234
BKA16	904	152	NA
Irkutsk			
BKA17	3317	618	NA
BKA18	1810	526	NA
BKA19	1821	389	NA
Lake Baikal			
BK2	950	710	ND ^c
BK3	1100	640	ND
BK4	960	460	ND
BK5	730	70	ND
BK6	810	790	ND
BK7	680	330	ND
Rivers			
BK1	2580	920	ND
BK8	3890	640	ND
BK9	4150	ND	ND
BK10	4340	698	ND

^a Not all air samples were analyzed for HCHs and HCB due to breakthrough at high sample volume. ^b NA, not available due to excessive breakthrough. ^c ND, not detected.

was officially approved for use in agriculture as a pre-emergence insecticide. HCH was also approved for use on beets, sunflowers, corn, and soybeans during the entire planting season. Soybean is a major crop in southern Siberia and far eastern Russia (2). Possible sources of HCH to Baikal are thus local, regional, and long-range atmospheric transport.

Results from air samples collected aboard the R/V *Vereshchagin* and from the Lystvianka Hydromet station are listed in Table 2 and averaged 489 ± 275 and 105 ± 65 pg m⁻³ for α - and γ -HCH, respectively ($n = 12$). These values also fall within the range of air concentrations measured at Lake Baikal 1 year later (6) where α -HCH ranged from 170 to 780 pg m⁻³ and γ -HCH ranged from 44 to 180 pg m⁻³. HCH concentrations in Irkutsk were higher than those found over the lake (1760–3320 and 386–612 pg m⁻³ for α - and γ -HCH, $n = 3$). This suggests current or recent use of HCH in areas surrounding Irkutsk. A comparison of mean α - and γ -HCH levels in air over Baikal and Irkutsk to values from regions that should reflect long-range transport only is shown in Figure 2 (9, 13, 16). Atmospheric concentrations of HCHs over Baikal are 2–3 times higher than those found in the Great Lakes (9), the Bering and Chukchi Seas (16), or the Arctic (13). This may be due to local transport from Irkutsk or local agricultural activity, or from a more distant source region.

The ratio of the α - and γ -isomers of HCH in air is often a clue to estimating the source or age of this pesticide. The ratio of α/γ within the technical formulation ranges from

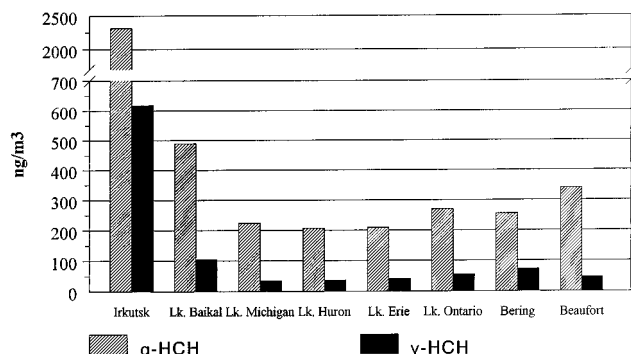


FIGURE 2. Comparison of mean HCH air concentrations (pg m^{-3}) over Lake Baikal ($n = 16$) and Irkutsk ($n = 3$) (June 1991, this work) with four lower Great Lakes [August 1990 (14)] and Arctic waters [August 1988, Bering and Chukchi Seas (21); June 1987, Beaufort Sea (18)].

4 to 15 (17). The range of the α/γ ratio observed in the air over Baikal is 4.6–5.8 and 4.5 over Irkutsk; thus, the source of HCHs to both areas is probably technical HCH. This suggests that technical HCH was or is used in the Baikal region. However, an α/γ ratio as low as 1.5 was observed in Baikal air in 1992 (6); therefore, lindane may also be an important source of HCH to the region.

The results of low-volume water sample are listed in Table 2. The mean concentrations of α - and γ -HCH in Baikal surface water were 827 ± 187 and $514 \pm 249 \text{ pg L}^{-1}$, respectively, and the average δ -HCH percent recovery was $83\% \pm 32\%$ ($n = 7$). Using the high-volume XAD-2 method ($n = 7$) α -HCH = 1054 ± 82 and γ -HCH = $239 \pm 27 \text{ pg L}^{-1}$, with a matrix spike recovery of γ -HCH of 82% (average of two values) (10). Reasons for the differences in γ -HCH concentrations are not apparent as both methods have good collection efficiency for this compound. The combined LV and HV average concentration of HCH in Baikal surface water (α -HCH = 941 ± 182 and γ -HCH = $400 \pm 233 \text{ pg L}^{-1}$) are the values used in subsequent flux calculations. Iwata et al. (6) observed lower HCH concentrations in 1992 (α -HCH = $36\text{--}760 \text{ pg L}^{-1}$ and γ -HCH = $18\text{--}200 \text{ pg L}^{-1}$) using an XAD-2 resin method with a 20-L sample volume. The differences between results from these two studies may be a result of the change in seasons. As suggested by Iwata (6), their study was conducted during early spring (May 14–June 1) before the ice at the surface of the lake had completely melted. Our study was conducted after the spring melt period (June 6–28). Higher water concentrations at the surface of Lake Baikal may be due to a combination of surface and riverine inputs and atmospheric deposition after the surface ice melted.

Measurements of HCHs from Baikal, the mouths of the Selenga and Upper Angara Rivers, and various freshwaters are compared in Figure 3. Baikal HCHs are similar to concentrations found in Great Lakes water in August 1990 (Figure 3) (9). α -HCH was 3–4 times higher in the Upper Angara (2600 pg/L , $n = 1$) and Selenga ($4100 \pm 200 \text{ pg/L}$, $n = 3$) Rivers (Figure 1) as compared to the open lake. The Upper Angara and Selenga Rivers run through mountainous regions, and increased HCHs may be due to runoff following spring snowmelt. Low Henry's law values [0.66 and $0.31 \text{ Pa m}^{-3} \text{ mol}^{-1}$ at 23°C for α -HCH and γ -HCH, respectively (18)] allow HCH to be scavenged from the air by precipitation. Concentrations found in the Selenga and Upper Angara Rivers are similar to those observed in Northern Ontario rivers and the St. Lawrence River (19) (Figure 3).

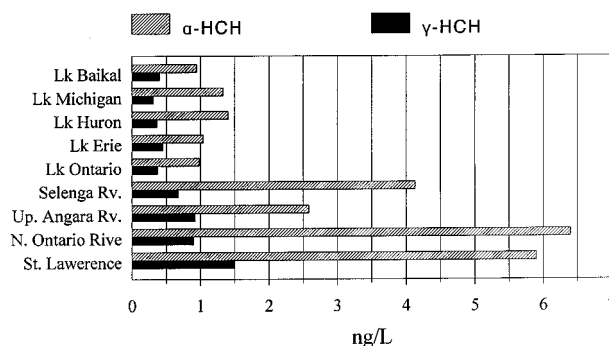


FIGURE 3. Comparison of mean HCH water concentrations (ng L^{-1}) from Lake Baikal ($n = 13$) and Selenga and Upper Angara Rivers ($n = 4$) (June 1991, this work) with the four lower Great Lakes [August 1990 (14)], northern Ontario Rivers, and St. Lawrence River (24).

More study of riverine inputs of HCHs and other organochlorines to Lake Baikal are required to determine their importance in the overall pollutant budget.

Chlordane. Chlordane is a mixture of about 120 compounds containing 6–12 chlorines (20, 21). In the United States 4500–5400 t of chlordane was used mainly as a termiticide from the early 1950s until it was phased out in the early 1980s and banned in 1988 (22). Known as chlorendane in the Soviet Union, it was used as a technical formulation of 60–75% *cis*- and *trans*-chlordane isomers and 25–30% related compounds including heptachlor and *cis*- and *trans*-nonachlor. Because of its extremely toxic nature, chlordane usage in the Soviet Union was very low and only under restricted conditions (1). Heptachlor was also used as a replacement for lindane due to its stability in alkaline soils and its lower cost. However, due to its toxic effects, the use of heptachlor was also limited (1).

Chlordane concentrations in air were quite low over Baikal and Irkutsk with means ranging from 0.14 pg m^{-3} for *cis*-nonachlor (CN) and 2.1 pg m^{-3} for *cis*-chlordane (CC) (Table 3). *cis*-Chlordane was the dominant constituent of the chlordane mixture in each sample with a mean concentration of 2.1 pg m^{-3} , followed by *trans*-nonachlor (TN), *trans*-chlordane (TC), and *cis*-nonachlor at 1.5, 1.2, and 0.14 pg m^{-3} , respectively. This is in general agreement with levels found in the Bering and Chukchi Seas ($\text{TC} + \text{CC} + \text{TN} + \text{CN} = \Sigma\text{Chlor} = 6.8 \text{ pg m}^{-3}$) (16) and in the Beaufort Sea (June 1987 $\Sigma\text{Chlor} = 10.7 \text{ pg m}^{-3}$) (13), and Alert, NT, Canada (March 1988, $\Sigma\text{Chlor} = 3.9 \text{ pg m}^{-3}$) (23). This indicates that in Baikal and Irkutsk, as in Arctic regions, chlordanes are present due to long-range transport. Average dissolved concentrations of chlordanes in Lake Baikal water were 14, 8.9, and 4.3 pg L^{-1} for *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor, respectively (10). *cis*-Nonachlor concentrations in water were below the limit of detection. Concentrations observed in both air and water were in close agreement to those found in 1992 by Iwata et al. (6).

DDT. DDT was used heavily in the Soviet Union during the 1960s and early 1970s. However, by 1974 the use of DDT was banned or heavily restricted (1). Some unofficial use of DDT may continue for insect control in remote areas of Siberia. Two DDT isomers (2,4'-DDT and 4,4'-DDT) and a metabolite (4,4'-DDE) were determined in air (Table 3). As with the HCHs, average ΣDDT (2,4'-DDT + 4,4'-DDT + 4,4'-DDE) concentrations in air over Irkutsk (128 pg m^{-3}) were higher than those found over Baikal (21.7 pg m^{-3}), suggesting a local source. Similar levels in air over Baikal

TABLE 3

Concentrations of Organochlorine Compounds in Baikal Air (pg m^{-3})

sample	TC	CC	TN	CN	4,4'-DDT	2,4'-DDT	4,4'-DDE	CHB	ΣPCB
<i>R/V Vereshchagin</i>									
BAKA1+4 ^a	3.8	6.3	1.6	NA ^b	2.9	4.2	1.9	NA	NA
BAKA2+3 ^a	5.0	5.2	6.0	NA	6.3	7.3	4.0	NA	NA
\bar{x}	4.4	5.8	3.8		4.6	5.8	3.0		
<i>Lystvianka Hydromet Station</i>									
BAKA5	2.9	2.9	2.5	0.18	15	8.6	14	19	266
BAKA6	1.2	1.9	1.6	0.15	7	4.5	5.3	15	150
BAKA7	0.07	2.8	1.1	0.15	5.9	5	5.9	11	253
BAKA11	0.74	1.5	1.2	0.09	3.6	2.6	1.7	16	113
BAKA16	0.67	1.2	1.1	0.13	10	8.5	11	11	200
$\bar{x} \pm \text{SD}^c$	1.2 ± 0.95	2.1 ± 0.76	1.5 ± 0.59	0.14 ± 0.03	8.3 ± 4.4	5.9 ± 2.6	7.5 ± 4.8	14 ± 3.5	196 ± 65
<i>Irkutsk, Limnological Institute Site</i>									
BAKA17	1.7	1.8	1.5	0.28	35	40	22	21	1387
BAKA18	1.7	4.0	1.7	0.2	66	41	38	20	1371
BAKA19	NA	NA	NA	NA	NA	NA	NA	NA	1213
$\bar{x} \pm \text{SD}$	1.7	2.9 ± 1.6	1.6 ± 0.18	0.24 ± 0.06	51 ± 22	47 ± 10	30 ± 12	21 ± 0.55	1324 ± 96

^a Extracts from samples were combined for organochlorine and PCB analysis and were analyzed separately for HCHs and HCB. ^b NA, not analyzed. ^c SD, standard deviation.

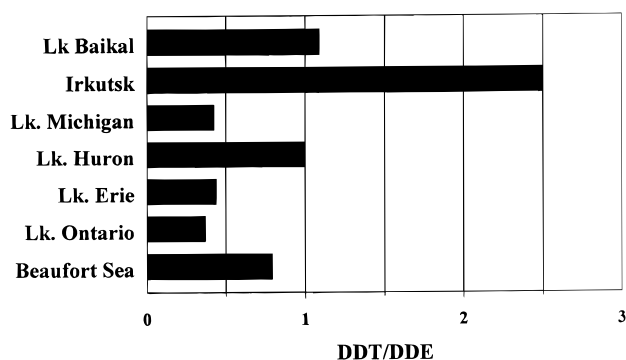


FIGURE 4. Ratio of 4,4'-DDT/4,4'-DDE in air (pg m^{-3}) over Lake Baikal, Irkutsk (June 1991, this work), the four lower Great Lakes [August 1990 (14)], and the Beaufort Sea [June 1987 (18)].

were also observed in 1992 by Iwata et al. (6) ($4,4'$ -DDE = 3.0 – 18 pg m^{-3} , $4,4'$ -DDT = 10 – 29 pg m^{-3}). In comparison, Lake Baikal ΣDDT values seem to be some where in between global background or Arctic levels ($4,4'$ -DDT + $4,4'$ -DDE = 5.2 pg m^{-3}) (13) and those observed over the Great Lakes (mean of four lower Great Lakes, $4,4'$ -DDT + $4,4'$ -DDE = 123 pg m^{-3}) (12).

The ratio of $4,4'$ -DDT/ $4,4'$ -DDE in air can be used as an indicator of the "age" of DDT (24). Experiments have shown that approximately 66% of DDT applied to fields is transformed to DDE within 1 year (25); however, transformation rates are extremely soil specific and can be highly variable. DDT/DDE ratios for the Great lakes (12) and the Beaufort Sea (13) are all ≤ 1 , suggesting that the DDT source to these area has been transformed to some extent (Figure 4). Baikal and especially Irkutsk air both have DDT/DDE ratios > 1 , suggesting a less aged source of DDT in Siberia. While elevated levels in Irkutsk air as compared to Baikal suggest local usage, surrounding countries may also contribute DDT to Baikal through long-range atmospheric transport. The Indian Department of Chemicals and Petrochemicals has reported 990 000 t of DDT was used in India from 1970 to 1993 (26). Average dissolved concentrations of DDT in Baikal surface waters were 31, 12, and 3.6 pg L^{-1} for $4,4'$ -DDT, $2,4'$ -DDT, and $4,4'$ -DDE, respectively. Sample-specific concentrations in water are given elsewhere (10).

HCB. As of 1974, HCB was used in the Soviet Union in combination with lindane and mercury-based fungicides as a seed dressing; however, overall use of this compound was low (27). HCB has been manufactured for use as a pesticide in the United States; however, it is normally released during the manufacture of several chlorinated industrial chemicals (28). This chemical is believed to be extremely persistent in the environment with an atmospheric lifetime of ≈ 80 days due to reaction with hydroxyl radicals (29). Individual sample results are listed in Table 2. The mean HCB concentration in the air over Baikal was $194 \pm 47 \text{ pg m}^{-3}$. However, HCB could not be determined in Irkutsk air since larger air volumes were collected and breakthrough to the second foam plug was substantial. Iwata et al. (6) found slightly lower levels ranging from 70 to 170 pg m^{-3} . Results were similar to Green Bay, WI ($160 \pm 87 \text{ pg m}^{-3}$) (12), Georgetown, SC ($120 \pm 40 \text{ pg m}^{-3}$) (12), Glendora, CA ($76 \pm 20 \text{ pg m}^{-3}$) (31), Point Petre, ON, Canada ($71 \pm 16 \text{ pg m}^{-3}$) (30), and Alert, NT, Canada ($153 \pm 32 \text{ pg m}^{-3}$) (23). The similarity of levels in such diverse regions attests to the persistence of HCB in the atmosphere, and for Baikal indicates a long-range atmospheric transport source. Surface water concentration averaged 20 pg L^{-1} in the dissolved phase (10).

Chlorinated Bornanes (Toxaphene). Global chlorinated bornane (CHB) production was 450 000–500 000 t from 1947 to 1977 (24, 32–33). Relative compositions of formulations differ (34); however, samples in this study were quantified against a technical toxaphene standard (Hercules Chemical). Findings of CHB residues in the Arctic Ocean ecosystem (35) illustrates the persistence of this pesticide in the environment. Polychlorinated terpenes with a chlorine content of approximately 55% were initially used in the Soviet Union for control of animal-borne parasites (2). Later, polychlorocamphene or toxaphene was introduced and, in 1987, was still widely used in Russian agriculture. The recommended formulation contained 50% polychlorocamphene, 30% transformer oil, and 15% emulsifier at an application rate of 3 kg of 0.5% active ingredient emulsion/ha, and total usage within the Soviet Union was 10 000–100 000 t. Soviet regulations allowed air concentrations of polychlorocamphene over a treated field of up

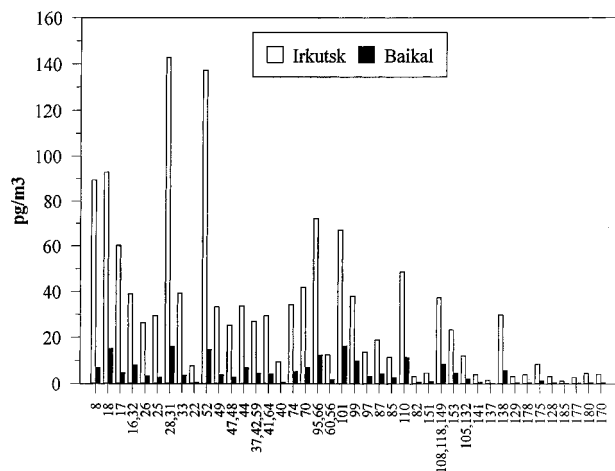


FIGURE 5. Comparison of PCB congener concentrations in air over Lake Baikal and Irkutsk.

to 0.5 mg/m³ (2). As of 1992, polychlorocamphene was categorized as a "severely restricted" pesticide (33).

CHB concentrations were similar in Baikal and Irkutsk air and ranged from 11 to 21 pg m⁻³ (Table 3). These concentrations were close to those over the Arctic Ocean (7.0–32 pg m⁻³) (23) and the Bering/Chukchi Seas (30–49 pg m⁻³) (16) in the late 1980s, regions influenced only by long-range transport. CHB concentrations in surface water averaged 64 ± 37 pg/L (10). A detailed discussion of CHBs in the air and water of Lake Baikal is given elsewhere (36, 37).

Polychlorinated Biphenyls. In the former Soviet Union, a technical mixture of PCBs called Sovol was mixed in different proportions with trichlorobenzenes. Sovol is similar in composition to Aroclor 1254. Total Sovol production between 1940 and the 1990s is estimated at approximately 100 000 t (38). A product called trichlorodiphenyl was manufactured from the late 1960s until the 1980s (total production estimated at 25 000 t) and is similar in composition to Aroclor 1242 (38). It is likely that an industrial region like the Angara River may be burdened with many used capacitors and transformers.

The congener patterns of PCBs in air over Baikal and Irkutsk were similar. The mean congener-specific concentrations for both locations are shown in Figure 5. Overall, the congener profile is dominated by the lower chlorinated congeners, and congeners 18, 28, 31, 52, and 101 were the three largest congeners found at both sites. Congeners 28 and 31 are the largest component of the trichlorodiphenyl mixture, and both congeners 18 and 52 are also significant components (38). Congeners 52 and 101, while relatively small in 1254, are important components of the Sovol mixture (38). This suggests that the source of PCBs to the atmosphere in this region is a mixture of trichlorodiphenyl and Sovol.

Total PCB (Σ PCB) concentrations from the Lystvianka Hydromet station are listed in Table 3 and ranged from 113 to 226 pg m⁻³, and in Irkutsk, PCB concentrations were approximately a factor of 10 higher and ranged from 1213 to 1387 pg m⁻³. Iwata et al. (6) observed much lower levels of PCBs in air over Baikal (8.7–23 pg m⁻³). This may be due to lower air and soil temperature conditions during the 1992 study. Hoff et al. (39) and Hornbuckle et al. (40) observed increased concentrations on airborne PCBs with increased air temperature during studies at Lakes Ontario and Michigan, respectively. A comparison of average

TABLE 4

Selected Henry's Law Constants and Temperature-Adjusted Values

compound	literature H (Pa m ³ mol ⁻¹)		ref	H , adjusted to 3.5 °C ^a
	value	temp (°C)		
α -HCH	0.66	23	23	0.14
γ -HCH	0.31	23	23	0.085
HCB	170	25	47	37
chlordane	6.6	23	50	1.0
4,4'-DDT	1.2	23	50	0.18
4,4'-DDE	7.95	20	52	1.6
CHB	0.62	20	51	0.13
PCB congeners, IUPAC Number				
25	17	25	48	3.5
28, 31	20	25	48	4.2
52	20	25	48	4.0
49	21	25	48	4.2
44	12	25	48	2.5
37, 42, 59	10	25	48	2.0
41, 64	14	25	48	2.8
74	10	25	48	2.0
70	10	25	48	2.0
95, 66	12	25	48	1.6
60, 56	8.2	25	48	2.7
101	9.0	25	48	1.2
99	7.9	25	48	1.0
97	7.5	25	48	0.97
87	6.0	25	48	0.77
110	6.0	25	48	0.77
151	6.0	25	48	0.77
118, 149	5.1	25	48	0.65
153, 105, 132	2.4	25	48	0.31
141, 179	6.5	25	48	0.84
138	1.5	25	48	0.20
129, 178	2.3	25	48	0.30
180	1.0	25	48	0.13

^a H values were adjusted for the measured temperature using the following slope values: α -HCH = -2810; γ -HCH = -2384 (23); HCB = -2492 (47); tri- and tetrachlorobiphenyls = -2628 and -2689, respectively (47); heavier PCBs = -3416 (49); chlordanes, DDT, and CHBs all = -3416 (49).

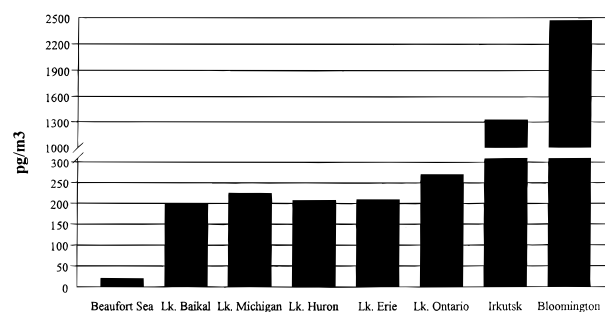


FIGURE 6. Comparison of Σ PCB concentrations in air (pg m⁻³) over Lake Baikal, Irkutsk (June 1991, this work), the four lower Great Lakes [August 1990 (14)], Beaufort Sea [June 1987 (18)], and Bloomington, IN [1986–1988, average of geometric means from three sites near heavy PCB contamination (44)].

Σ PCBs in Irkutsk and Baikal air with levels measured in urban and remote regions is given in Figure 6. Σ PCB concentrations in air over Lake Baikal are higher than those found in the Canadian Arctic (13), but are similar to the four lower Great Lakes (12) (regions affected by atmospheric transport from large urban areas). Concentrations found in Irkutsk air are within a factor of 2 of Bloomington, IN (41), an area in close proximity to several PCB-contaminated sites. Recent measurements at the Bloomington site compared with the 1986–1987 measurements showed that concentrations of PCBs in air had not decreased after 6

years (42). Therefore, the suspected PCB contamination of the Irkutsk region may be a continuing atmospheric source of PCBs to Lake Baikal.

The average concentration of Σ PCB in Baikal surface waters was 560 ± 180 pg/L in the dissolved phase and 420 ± 400 pg/L in the particle-bound phase (10) with higher concentrations observed in the southern basin than in the northern and central basins. Similar concentrations and trends were observed by Iwata et al. (6) in their 1992 study. The congener profile observed within the water column is quite different than that observed in the air. The largest components of the water column congener profile were 101, 110, and 118+149 (penta- and hexachlorobiphenyls) while the largest components of the air sample profile were tri-, tetra-, and pentachlorobiphenyls. As observed by Kucklick et al. (10), the Baikal surface water congener profile is also quite different than that observed in Lake Superior where the atmosphere is the major source of PCBs. This suggests that run-off of Sovol-contaminated soils from the large industrial region on the southern end of the lake may be the dominant source of PCBs entering the water column of Lake Baikal.

Air–Water Gas Exchange

Theoretical Approach. The air–water partition coefficient of a chemical, K_H , is equal to the ratio of the air and water concentrations at equilibrium. The Henry's law constant, H , in units of $\text{Pa m}^3 \text{mol}^{-1}$ is used within the fugacity-based flux calculations where $K_H = H/RT$. R is the universal gas constant ($\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$), and T is the water temperature in units of K. Log H varies linearly with $1/T$; however, most H values for pesticides have been reported at only a single temperature, i.e., 20–25 °C. Henry's law constants have been determined experimentally as functions of temperature, however, for α - and γ -HCH (18), HCB (43), and a few PCBs (44). In this work, H values were adjusted to the temperature of Lake Baikal water (3.5 °C), and values of the slope were taken as -2810 and -2384 for α - and γ -HCH (18), -2492 for HCB (44), -2628 and -2689 for tri- and tetrachlorobiphenyls (43), and -3416 for heavier PCB congeners (45). A slope of -3416 was also assumed for chlordanes, nonachlors, DDT, DDE, and CHBs. A list of selected literature values for H and temperature-adjusted values used within flux calculations is given in Table 4 (18, 43, 44, 46–48). The net flux of each pesticide was calculated by the two-film model using fugacity-based definitions as described in Mackay (49) and others (50). Mass-transfer coefficients for air and water were calculated according to the models of Mackay and Yuen (51).

Results. Gas exchange fluxes can vary widely from hour to hour with changes in air concentrations and wind speed. High wind speed events such as storms are probably important contributors to the overall flux. Daily flux measurement at several stations around the lake over an extended period would be the most desirable type of data set, but restrictions on time and resources limit the spatial and temporal resolution of results. Since detailed wind speed measurements are not available, the average air and water concentrations (Table 5), temperature, and wind speed were used to estimate the fugacity ratio and flux for each compound. The average wind speed was low at 3.0 m s^{-1} , the average surface water temperature was 3.5 °C, and the average air temperature was 12 °C.

Values for air-phase and water-phase Schmidt numbers, Sc_a and Sc_w , increased with molecular weight. The range

TABLE 5

Flux Calculations for Organochlorine Pesticides and PCBs in Lake Baikal^a

compound	C_w (pg/L)	C_a (pg/m ³)	D_v (mol Pa ⁻¹ m ⁻² h ⁻¹)	Γ f_w/f_a	N (ng/m ² day)
a-HCH	941	489	0.114	0.12	-112
g-HCH	400	105	0.114	0.14	-24
HCB	20	194	0.107	1.67	32
TC	14	1.2	0.105	5.36	1.2
CC	9	2.1	0.105	1.94	0.46
TN	4	1.5	0.105	1.28	0.10
2,4'-DDT	12	5.9	0.104	0.16	-1.2
4,4'-DDT	31	8.3	0.104	0.30	-1.4
4,4'-DDE	3.6	7.5	0.104	0.34	-1.2
CHB	64	14	0.103	0.25	-2.5
PCB 25	18	2.6	0.113	11	7.4
PCB 28, 31	13	16	0.113	1.5	2.2
PCB 52	22	15	0.111	2.7	6.2
PCB 49	29	3.8	0.111	14	13
PCB 44	24	6.8	0.111	3.8	4.9
PCB 37, 42	15.9	4.3	0.112	3.2	2.6
PCB 41, 64	26.4	4.1	0.111	8.0	7.3
PCB 74	5.01	5.2	0.111	0.85	0.20
PCB 70	13.1	6.9	0.109	1.7	1.1
PCB 95, 66	24.1	12.4	0.110	1.3	1.0
PCB 60, 56	7.55	1.9	0.111	4.7	1.8
PCB 101	34.8	16.3	0.109	1.1	0.30
PCB 99	19.8	9.7	0.109	0.90	-0.22
PCB 97	10.0	3.2	0.109	1.3	0.22
PCB 87	10.2	4.2	0.110	0.82	-0.17
PCB 110	43.3	11.3	0.110	1.3	0.71
PCB 151	5.3	1.1	0.109	1.6	0.14
PCB 118, 149	45.4	8.3	0.109	1.6	1.0
PCB 153, 105, 132	32.0	9.2	0.110	0.47	-1.1
PCB 138	25.7	5.6	0.109	0.39	-0.68
PCB 129, 178	2.7	1.0	0.109	0.35	-0.13
PCB 180	2.0	0.5	0.108	0.22	-0.070

^a C_w , average surface water concentration; C_a , average air concentration; Γ , fugacity gradient; D_v , transport parameter; N , net flux across the air–water interface. A negative value of N denotes a depositional or air-to-water flux. A positive N value denotes a net volatilization or water-to-air flux (53).

of Sc_a for pesticides was 2.62 for HCB to 3.3 for CHBs and 2.67–3.04 for PCBs. For Sc_w , the range for pesticides was 4580 for HCB to 6110 for CHBs (12) and 3025–3638 for PCBs. Values for the fugacity gradient and air-to-water flux for each compound are given in Table 5. While fluxes derived from average conditions do not represent real average fluxes, results may be considered a lower limit and reveal overall trends. Iwata et al. (6) also estimated flux values for organochlorine pesticides and selected PCB congeners. However, $Sc_a = 2.0$ and $Sc_w = 1000$ were used for each compound, and different H values were selected from some compounds. Also, fluxes were calculated for 0, 5, and 10 m s^{-1} wind speeds. Despite these differences, flux values from our study fell within the range of values reported for the 5 m s^{-1} wind speed from the Iwata et al. (6) report.

The fugacity gradient (Γ), or the ratio of the measured fugacity in water and air, is a measure of the how close the two phases are from being at equilibrium. A fugacity gradient of 1 indicates equilibrium, a value less than 1 indicates that the net flux direction will be from air to water, and a value greater than 1 indicates the net flux will be from water to air. In Baikal, the α - and γ -HCH fugacity gradients were similar and well below 1.0 (α -HCH = 0.12 and γ -HCH = 0.14). Similar conditions were observed in Green Bay, Lake Michigan during spring 1989 (14) where

$\Gamma = 0.31$ and 0.17 for α - and γ -HCH, respectively. In both Baikal and Green Bay, the water was "under saturated" with respect to the air, and the flux direction is from air to water. Deposition conditions were also found in the Bering and Chukchi Seas (16) and in the Beaufort Sea (13) where Γ ranged from 0.6 to 0.78 in the case of α -HCH and from 0.30 to 0.40 for γ -HCH. In the Selenga River, however, higher water concentrations and water temperatures resulted in $\Gamma = 1.5$ for α -HCH and 0.68 for γ -HCH.

Depositional fluxes were estimated at 112 and 24 $\text{ng m}^{-2} \text{d}^{-1}$ for α -HCH and γ -HCH, respectively. This flux would contribute 3.5 kg d^{-1} for α -HCH and 0.74 kg d^{-1} of γ -HCH to the lake surface waters (surface area of Baikal = $31\,500$ km^2). Low Henry's law values and low water temperatures in the lake surface water contributed to $\Gamma < 1$ for the DDTs ($2,4'$ -DDT = 0.16 , $4,4'$ -DDT = 0.30 , and $4,4'$ -DDE = 0.34) and CHB (0.25) as well. Deposition fluxes were lower in magnitude than the HCHs due to lower overall concentrations with $2,4'$ -DDT + $4,4'$ -DDT + $4,4'$ -DDE = 3.7 $\text{ng m}^{-2} \text{d}^{-1}$ and CHB = 2.5 $\text{ng m}^{-2} \text{d}^{-1}$. Cotham and Bidleman (52) estimated that the flux of $4,4'$ -DDT and CHB to the Canadian Arctic during the summer months would be 0.5 and 6.7 $\text{ng m}^{-2} \text{d}^{-1}$, respectively. Low air concentrations of chlordane contributed to values of $\Gamma > 1$ (volatilization) for all three isomers (Table 5), particularly TC. Flux values are small; however, ΣChlor flux = 1.8 $\text{ng m}^{-2} \text{d}^{-1}$ and would amount to a loss of only 57 g of ΣChlor /day over the entire lake's surface. The fugacity gradient value for HCB was also >1 due to its high H value (37 $\text{Pa m}^3 \text{mol}^{-1}$) resulting in a volatile flux of 32 $\text{ng m}^{-2} \text{d}^{-1}$.

PCBs have relatively high H values, and despite low water temperatures, $\Gamma > 1$ for all tri- and tetrachlorinated biphenyls as well as some penta- and hexachlorinated biphenyls (Table 5). Fluxes were estimated only for congeners above the LOD for all samples in both air and water. Flux values ranged from a volatilization flux of 13 $\text{ng m}^{-2} \text{d}^{-1}$ for congener 49 to a depositional flux of 1.1 $\text{ng m}^{-2} \text{d}^{-1}$ for congeners 153, 105, and 132. The sum of the net fluxes of all 22 congeners results in a volatile loss of 47 $\text{ng m}^{-2} \text{d}^{-1}$. This flux rate results in a loss of 1.5 g of ΣPCBs d^{-1} . Volatilization of PCBs from large, pristine, oligotrophic lakes has also been observed by Baker and Eisenreich (53) and Jeremiason et al. (54) in Lake Superior (19 and 63 $\text{ng m}^{-2} \text{d}^{-1}$, respectively, for 25 congeners); by Achman et al. (55) in Green Bay, Lake Michigan (13 – 1300 $\text{ng m}^{-2} \text{d}^{-1}$ for 85 congeners); and by Hornbuckle et al. (56) in Lake Michigan (24 – 220 $\text{ng m}^{-2} \text{d}^{-1}$ for 77 congeners).

While these fluxes are highly variable depending on changes in wind speed and air concentrations, the HCHs are probably deposited to the lake surface waters in the largest amounts by gas exchange as compared to the other compounds. An estimate of total loadings or volatilization of organochlorines and PCBs in Lake Baikal for the month of June 1991 is given in Figure 7. Gas exchange is, of course, only one pathway for atmospheric deposition. Other types of atmospheric deposition (precipitation, particle fallout) may be more significant for other pollutants as seen in the Arctic (52). An intensive study of air, lake water, tributaries, and precipitation is the only way to determine the contribution of atmospheric deposition to the Baikal pollutant budget.

Acknowledgments

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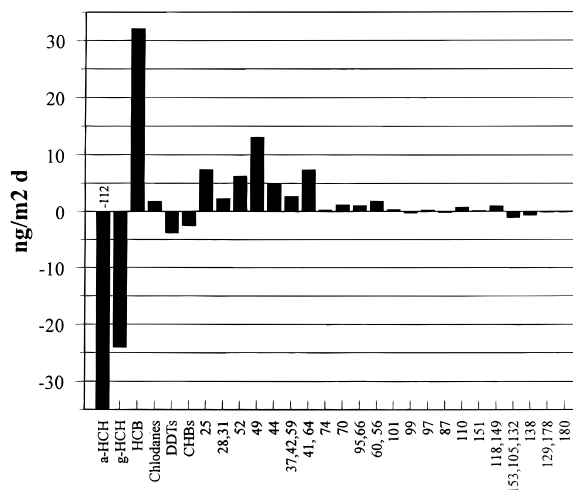


FIGURE 7. Net flux rate of organochlorine pesticides and PCB congeners across the air–water interface of Lake Baikal in June 1991 ($\text{ng m}^{-2} \text{d}^{-1}$).

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