Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments

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Supporting Information

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Decline of Pigment Manufacture in the US

Chemicals listed in the US Toxics Release Inventory (TRI) that are associated with diarylide yellow pigment manufacture are 3,3'-dichlorobenzidine and 3,3'-dichlorobenzidine dihydrochloric acid. The total on- and off-site disposal and other releases of these chemicals have declined dramatically. In 1988, 14 facilities in the US released nearly 100,000 kg of these chemicals. By 2001, the number of facilities had declined to 4, generating 49,000 kg of total releases. In 2011, only one facility was still using these chemicals, generating 5 kg of waste. Despite this rapid decline in the US, worldwide pigment use was growing steadily during these years due to the shift of manufacturing base to Asia.

Analytical Methods of PCBs

Paper samples

Paper samples were analyzed in year 2009 and 2013. The samples from 2009 were processed as described previously.[1] In brief, each sample (~5 g) was spiked with PCBs 14, 23, 65, and 166 (Cambridge Isotope Laboratories, Andover, MA) as surrogates and extracted by Soxhlet in dichloromethane for 24 h. The maximum temperature achieved during Soxhlet extraction was the boiling point of dichloromethane, 40 °C. Since diarylide yellow is reported to be able to withstand temperatures of up to 180 to 200°C, breakdown of diarylide yellow to form PCB 11 during the extraction process is unlikely. The extracts were then reduced in volume by rotary evaporation and fractionated on a column of 3% water-deactivated alumina (60-325 mesh, Fisher Scientific, Pittsburgh, PA). The PCB fraction was eluted with hexane, concentrated under a gentle stream of nitrogen gas to about 0.5 mL, and injected with internal standards containing PCBs 30 and 204 (Cambridge Isotope Laboratories, Andover, MA).

Paper samples of 2013 were extracted in 3~5 g by an accelerated solvent extraction system (ASE 200, Dionex, Sunnyvale, CA). The ASE was operated at 100 °C and 1500 psi using either hexane/dichloromethane (3:1, v/v) or hexane as the extraction solvent. Deuterated PCBs 65 and 159 (C/D/N Isotopes, Inc., Quebec, Canada) were added as surrogates. The extracts were cleaned up by either 3% water-deactivated alumina as described above or 2.5% water-deactivated florisil (60-100 mesh, Fisher Scientific, Pittsburgh, PA). PCBs were eluted with hexane on the alumina column and petroleum ether on the florisil column. The PCB fraction was concentrated to 0.5 mL and spiked with deuterated PCBs 30 and 116 (C/D/N Isotopes, Inc., Quebec, Canada) as internal standards.

Clothing

Samples of clothing were extracted either in ~5 g using a Soxhlet or in 1~2 g using an ASE system as described above. The ASE was operated at 100 °C and 1500 psi using hexane/dichloromethane (3:1, v/v) as the extraction solvent. Deuterated PCBs 65 and 159 were added as surrogates. Soxhlet extracts were split into halves with one of them being processed for further analysis. Samples were cleaned up with either 3% water-deactivated alumina or 2.5% water-deactivated florisil as described above. All PCB fractions were concentrated to 0.5 mL and spiked with deuterated PCBs 30 and 116 as internal standards. Some clothing samples were analyzed with two methods (i.e. ASE extraction with alumina cleanup vs. Soxhlet extraction with florisil cleanup). The levels of PCB 11 measured in the same materials did not vary significantly between the two methods (Table S1), indicating that the elevated temperature and pressure in the ASE does not cause breakdown of the pigment or additional release of PCB 11,[2] and that both cleanup methods are acceptable for clothing samples. Measured concentrations varied within a factor of two for the same fabric processed by both ASE-alumina and Soxhlet-florisil methods. This variation may be due in part to the natural variation in concentration in different parts of the garment. This variation is expected to be particularly large in garments with a printed textile design.

Leaching tests

Two Teflon columns were prepared: one packed with ~15 g of shredded paper samples and the other filled with clean XAD-2 resin (Amberlite, Dow Chemical, Midland, MI). MilliQ water was pumped from a plastic reservoir first through the sample column and then the XAD-2 column at a constant rate using a peristaltic pump (Masterflex L/S Easy Load II Pump, Cole-Parmer, Vernon Hills, IL). The test duration lasted approximately 48 hours. PCBs that leached from the sample column were sorbed by XAD-2 resin and thus leachate coming out of the XAD-2 column was free of PCBs. This was confirmed because no PCBs were detected in the leachate from the XAD-2 column; therefore, 2 L of MilliQ water was continuously pumped and reused throughout the test duration. Loaded XAD-2 resin was stored in acetone at 4 °C until extraction.

PCB analysis for XAD-2 resin resembled the procedure described previously.[3] Prior to extraction, all samples were injected with surrogates including either PCBs 14, 23, 65, and 166 or deuterated PCBs 65 and 159. Samples were Soxhlet extracted for 24 h in hexane/acetone (1:1, v/v) and then liquid-liquid extracted with 60 mL of Milli-Q water to separate the aqueous fraction from the organic fraction. The aqueous fraction was back-extracted three times with 50 mL of hexane and 1 g of NaCl in a separatory funnel. The extracts were then concentrated to ~ 1 mL and cleaned up on a 3% water-deactivated alumina column to collect the PCB fraction eluted with hexane. Finally the fraction was reduced in volume and injected with an internal standards containing either PCBs 30 and 204 or deuterated PCBs 30 and 116 for quantification.

GC/MS/MS analysis

Instrumental analysis of PCBs was performed by a gas chromatograph (6890N, Agilent, Santa Clara, CA) with a tandem quadrupole mass spectrometer (Quattro Micro GC, Waters, Milford, MA) by a modified EPA method 1668A as described previously.[4] It should be noted that either a DB-5 capillary column (60m×0.25mm× 0.25μm, Agilent Technologies, Santa Clara, CA) or an

SPB-Octyl capillary column (30m×0.25 mm×0.25μm, Sigma-Aldrich, St Louis, MO) was used for PCB analysis on the GC/MS/MS.

Temperature programs for both columns are specified as follows. For the DB-5 column, the initial oven temperature 70°C was increased at a rate of 7°C min^{-1} to 180°C, followed by 1.05°C min^{-1} to 225°C, then 5.75°C min^{-1} to 285°C, and 11.5°C min^{-1} to a final temperature of 300°C, holding for 20 min. For the SPB-Octyl column, the initial oven temperature was held at 75°C for 5 min, then increased at a rate of 15°C min^{-1} to 150°C, holding for 1 min, followed by 2.5°C min^{-1} to a final temperature of 280°C, holding for 3 min. The instrument was operated with an electron impact (EI) source under multiple reaction monitoring (MRM) mode. Ion transitions for each PCB homologue group are identical on both columns. PCB 11 was identified by monitoring the transition from precursor ion at m/z 222+224 to product ion at m/z 152 using authentic PCB 11 standard (Ultra Scientific, N. Kingstown, RI). The Frame solutions (Accustandard, Inc., New Haven, CT) containing all 209 PCB congeners were analyzed on both columns to confirm that no other di-CB congeners coeluted with PCB 11 in the chromatographic system. Internal standards PCB 30 or deuterated PCB 30 were used for quantification of PCB 11. Recoveries of surrogate standards PCB 23 or deuterated PCB 65 were reported for quality assurance.

Quality Assurance/Quality Control

Glass fiber filters (GFFs) or quartz fiber filters (QFFs) were analyzed as laboratory blanks for PCB 11 measurement in consumer goods. Pre-cleaned XAD-2 resin was used as the blank for leaching tests. GFFs and QFFs were baked at 450°C for 4 h prior to extraction. XAD-2 resins were Soxhlet extracted sequentially with methanol, acetone, hexane, acetone, and methanol for

24 h each and stored in MilliQ water before use. Teflon columns, tubings and cylinders were rinsed with methanol and MilliQ water prior to leaching tests. PCB 11 was below the detection limit in all laboratory blanks except three filter blanks. Recoveries of surrogate spiked onto paper samples ranged from 70% to 127 % for PCB 23 and from 49% to 78% for deuterated PCB 65. Surrogate recoveries of deuterated PCB 65 spiked onto clothing samples ranged from 22% to 122%. Recoveries of surrogate PCB 23 spiked onto selected XAD-2 resins ranged from 44% to 126%. Recoveries of the deuterated PCB 65 surrogate spiked onto XAD-2 resins ranged from 31% to 73%. PCB 11 concentrations were reported with correction by laboratory blanks and surrogate recoveries.

Mass Flow Analysis

Mass Flows Less Than 1 kg y^{-1}

Advection to the Atlantic Ocean

The median concentration of PCB 11 in Delaware River is about 15.6 pg L^{-1}. Based on 48 years of records collected by the USGS at Port Jervis, NY, the average flow of the Delaware River is 4,800 ft^3 s^{-1} or 1.2×10^{10} L d^{-1}.[5] Therefore, the mass flow of PCB 11 in the river under steady state is estimated to be 187 mg d^{-1} (0.068 kg y^{-1}).

Sedimentation via Particulate Matter

Sedimentation functions as a loss mechanism for PCB 11 in the Delaware River through burial into deeper layers of the sediment bed. In the Delaware River Total Maximum Daily Load (TMDL) model, two types of organic carbon were considered: biotic carbon (BIC) and particulate detrital carbon (PDC). Sedimentation of PCB 11 is expected to be primarily associated with PDC because its settling rate is much faster than that of BIC. The mass flow of

PCB 11 via settling of PDC into sediments (L_s, mg d^{-1}) is estimated by Eq. S1.

$$L_s = C_s \cdot A_s \cdot v_{PDC} \cdot C_{PDC,w}/1000 \qquad \text{(Eq. S1)}$$

where C_s is PCB 11 concentration in the sediments with a median of 30 pg g^{-1}; A_s is the water surface area around 2,000 km^2; v_{PDC} is the gross settling velocity of PDC that was assigned at 1 m d^{-1} in the water quality model developed by the Delaware River Basin Commission (DRBC);[6] and $C_{PDC,w}$ is PDC concentration in the water column ranging from 0 to 3.5 mg L^{-1}.[6] Therefore, the loss of PCB 11 via sedimentation was estimated to be from zero up to 210 mg d^{-1} or about 0.077 kg y^{-1}.

Removal via Sewage Sludge

The mass flow of PCB 11 sequestered in sewage sludge can be calculated from the removal efficiency of wastewater treatment plants (WWTPs). The input of PCB 11 into the WWTPs is roughly distributed between removal by sewer sludge and outflow with WWTP effluent. Removal efficiency of PCB 11 in WWTPs on the Delaware River is calculated to be between 63% to 94%.[7] We previously calculated that the load of PCB 11 from the top 12 discharger to the river totals about 190 mg d^{-1}.[1] Assuming an average removal efficiency of 80%, the mass flow of PCB 11 in sewage sludge is estimated as four times the effluent load of PCB 11 from the top 12 dischargers, or 760 mg d^{-1} (0.28 kg y^{-1}). Because the effluent load was calculated from geometric mean concentration and average daily flow rate, both measured by the dischargers, the uncertainty associated with this load estimate is relatively small and has been discussed earlier.[1]

Processes Assumed to Be Negligible

Reductive dechlorination of higher molecular weight PCBs (PCBs 77, 118, 126, 156 and 169) could lead to elevated concentration of PCB 11 under anaerobic conditions in sediments.[8-11] However, none of these potential precursors to PCB 11 are primary constituents in any Aroclor mixtures or in the environment. In addition, our previous study examined the concentration ratios of PCB 11 to PCB 4, a characteristic dechlorination end product, in the Delaware River and concluded that the source of PCB 11 is different from that of PCB 4.[1] Furthermore, we examined the congener patterns of PCBs that are formed from dechlorination in this watershed and found that PCB 11 was not a significant product.[12] Therefore, it is unlikely that reductive dechlorination of heavier PCBs is responsible for the prevalence of PCB 11 found in the environment.

PCB 11 may be susceptible to aerobic degradation. Although some recent studies have isolated certain bacterial strains capable of growing on dichlorobiphenyls including PCB 11,[13] most microorganisms characterized in aerobic degradation of PCBs are mostly associated with monochlorobiphenyls and their growth frequently requires support from additional carbon sources such as biphenyl. There is no convincing data that demonstrate substantial degradation of PCB 11 in the environment. If such degradation did occur, it would only widen the discrepancy between the calculated inflow and outflow/storage of PCB 11 in the Delaware River Basin.

Table S1. PCB 11 concentrations in fabric materials measured by different extraction-cleanup methods (ND = not detected, Limit of Detection (LOD) = 0.10 ng g^{-1}).

Fabric Sample	Material	Color	Type of Coloring	PCB 11 (ng g^{-1})		
				ASE-Alumina	Soxhlet -Florisil	ASE-Florisil
Lab blank (GFF)	glass fiber filter	white		ND		
Lab blank (QFF)	quartz fiber filter	white			ND	
Kid's white sock (A)	cotton/polyester/ spandex	white	dyed			1.1
Kid's white sock (B)	cotton/polyester/ spandex	white	dyed			2.2
Woman's white tank	cotton/ polyester	white	dyed	1.6		
Kid's white sweatshirt	cotton/ polyester	white	dyed	0.41		
Kid's pink knit shirt	cotton/ polyester	dark pink	dyed	1.0	0.45	
Kid's pink sock	acrylic/polyester/ spandex	dark pink	dyed	3.0	2.2	
Kid's yellow sock	acrylic/polyester/ spandex	yellow	dyed	1.7	3.1	
Kid's green sock	acrylic/polyester/ spandex	green	dyed	1.9		
Dish wash cloth	cotton	light yellow	dyed	0.27		
Baby's luncheon napkins (A)	cellulose	yellow/red	printed	79		
Baby's luncheon napkins (B)	cellulose	pink/white	printed	4.6		
Kid's pajamas (A)	polyester	yellow	printed	4.7	2.5	
Kid's pajamas (B) front	cotton	yellow	printed	14		
Kid's pajamas (B) back	cotton	red	dyed	0.62		
Kid's handkerchief	cotton	yellow	printed	57	72	
Kid's magic towel	cotton	yellow/ orange	printed	15		

Table S2. Properties of the bulk compartments and sub-compartments: volume fraction of sub-compartment, density, organic carbon (OC) fraction, volume, area and depth.

bulk compartment	sub-compartment volume fraction				bulk compartment density (kg/m^3)	fraction OC in solids	volume (m^3)	area (m^2)	depth (m)
	air	water	solids	biota					
AIR	1.0	0	2 x 10^{-11}	0	1.19		$1.8x10^{12}$ ~ $1.8x10^{13}$	3.5 x 10^{10}	50 ~ 500
WATER	0	1.0	5 x 10^{-6}	1 x 10^{-6}	1000	0.2	4.0 x 10^{10}	2.0 x 10^{9}	20
SOIL	0.2	0.3	0.5	0	1500	0.02	3.3 x 10^{9}	3.3 x 10^{10}	0.1
SEDIMENT	0	0.7	0.3	0	1420	0.04	2.0 x 10^{7}	2.0 x 10^{9}	0.01
sub-compartment density (kg/m^3)	1.19	1000	2400	1000					

Table S3. Transport parameters between bulk compartments (MTC = mass transfer coefficient).

transport parameter	value
AIR-WATER	
air-side MTC over water	3 m h^{-1}
water-side MTC	0.03 m h^{-1}
rain rate	9.7 x 10^{-5} m h^{-1}
scavenging ratio	200000
dry deposition velocity	10.8 m h^{-1}
AIR-SOIL	
air-side MTC over soil	1 m h^{-1}
diffusion path length in soil	0.05 m
molecular diffusivity in air	0.04 m^2 h^{-1}
molecular diffusivity in water	4.0 x 10^{-6} m^2 h^{-1}
WATER-SOIL	
solids runoff rate from soil	2.3 x 10^{-8} m h^{-1}
water runoff rate from soil	3.9 x 10^{-5} m h^{-1}
WATER-SEDIMENT	
water-side MTC over sediment	0.01 m h^{-1}
diffusion path length in sediment	0.005 m
molecular diffusivity in water	4.0 x 10^{-6} m^2 h^{-1}
sediment deposition rate	4.6 x 10^{-8} m h^{-1}

sediment resuspension rate	1.1×10^{-8} m h^{-1}

Table S4. Rates of advection and degradation in each bulk compartment.

bulk compartment	advection		degradation	
AIR	wind speed	4 m s^{-1}	rate constant	7.68×10^{-3} h^{-1}
	air transfer rate to stratosphere	0.01 m h^{-1}		
WATER	water flow rate	1.2×10^{10} L d^{-1}	rate constant	0
SOIL	leaching rate from soil to groundwater	3.9×10^{-5} m h^{-1}	rate constant	0
SEDIMENT	sediment burial rate	3.4×10^{-8} m h^{-1}	rate constant	0

Table S5. Physical-chemical properties of PCB 11 from US EPA's EPISuite.

property	value
molecular weight	223 g mol^{-1}
vapor pressure	0.0948 Pa
water solubility	1.046 g m^{-3}
octanol-water partition coefficient ($\log K_{ow}$)	5.27

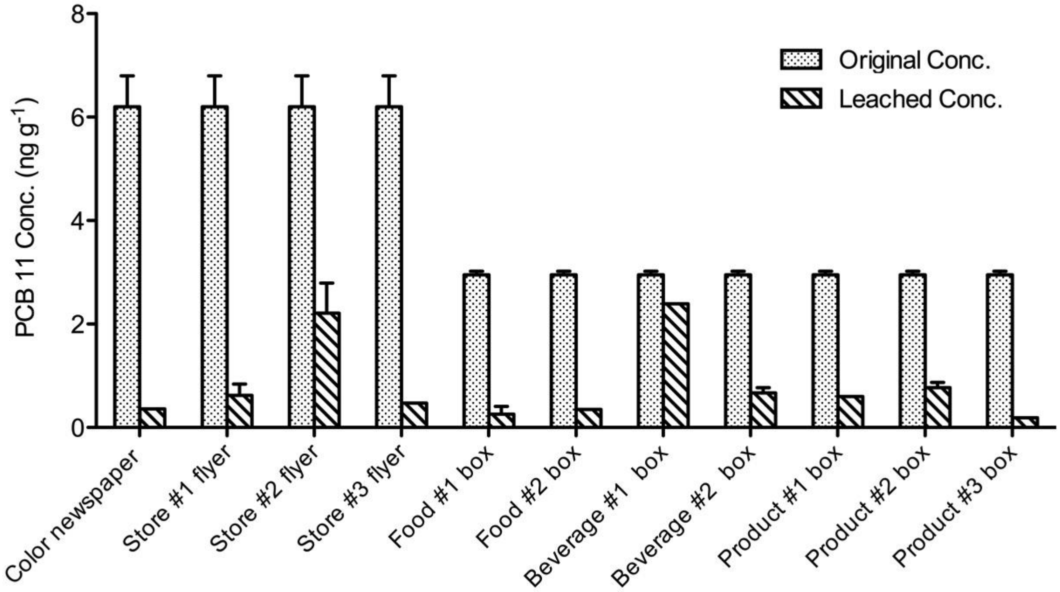
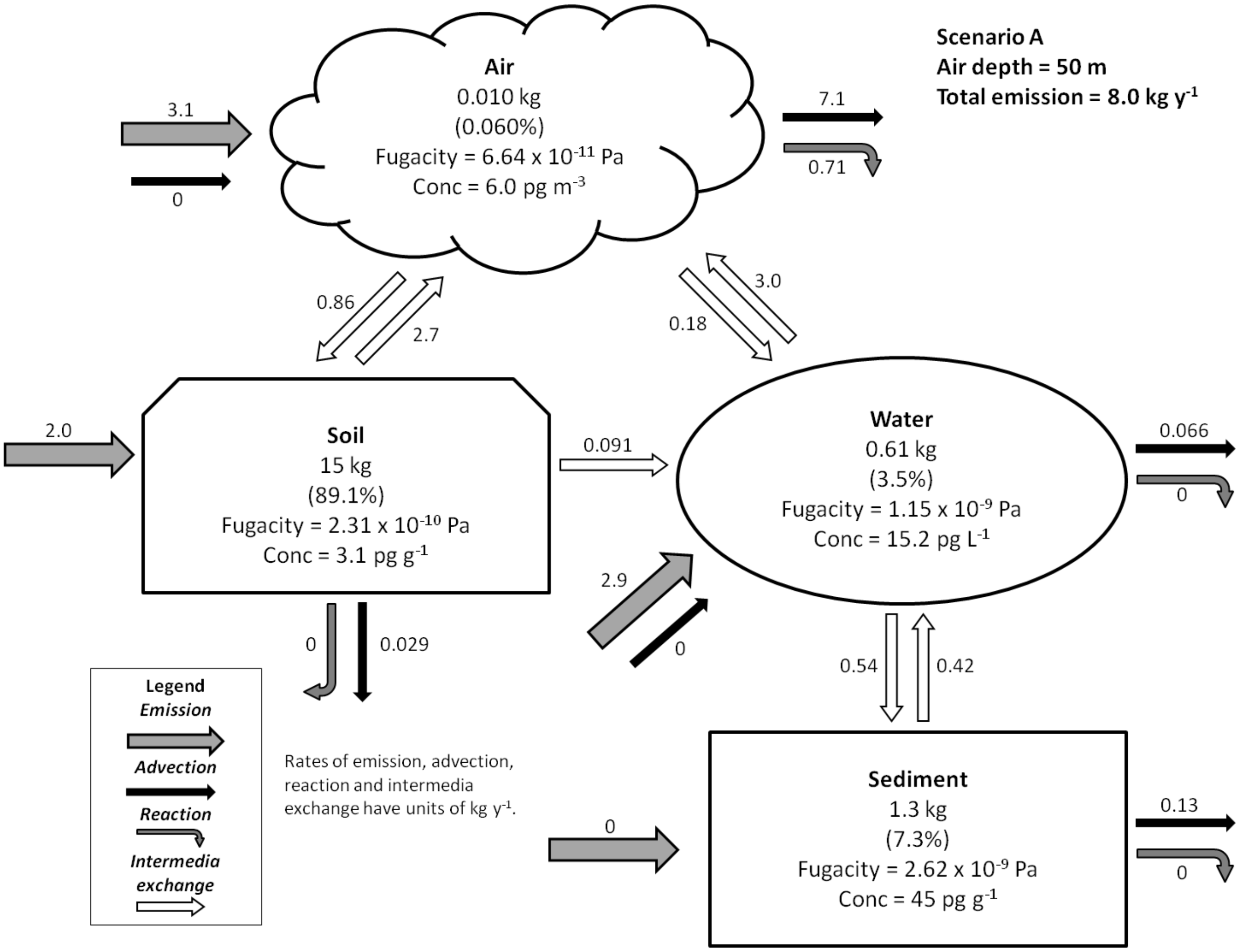
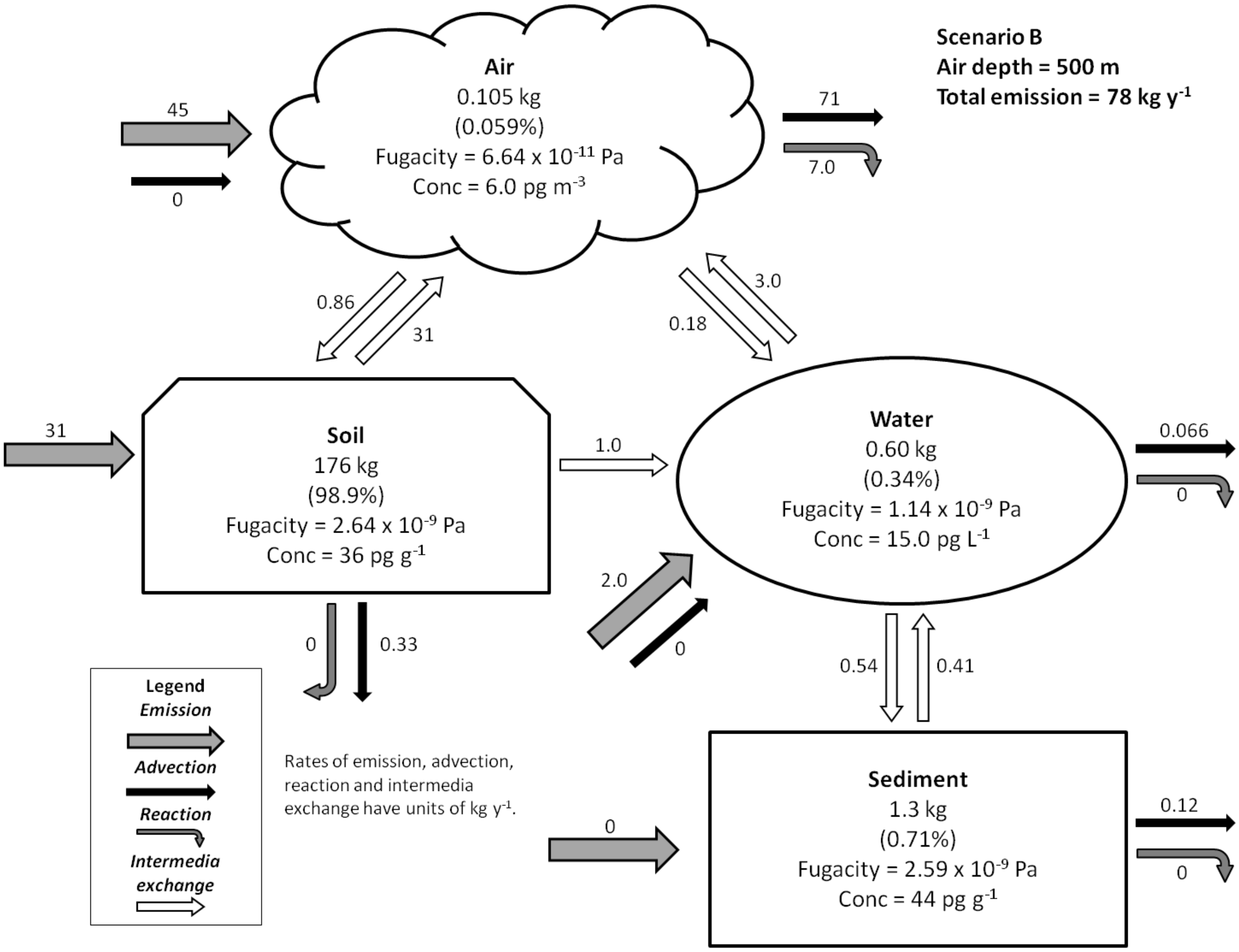


Figure S1. Original concentrations of PCB 11 (ng g^{-1}) in tested materials (dotted column) and leached concentrations of PCB 11 (ng g^{-1}) from respective materials (striped column). Error bar wherever displayed represents one standard deviation of measurements from multiple samples or leaching tests.



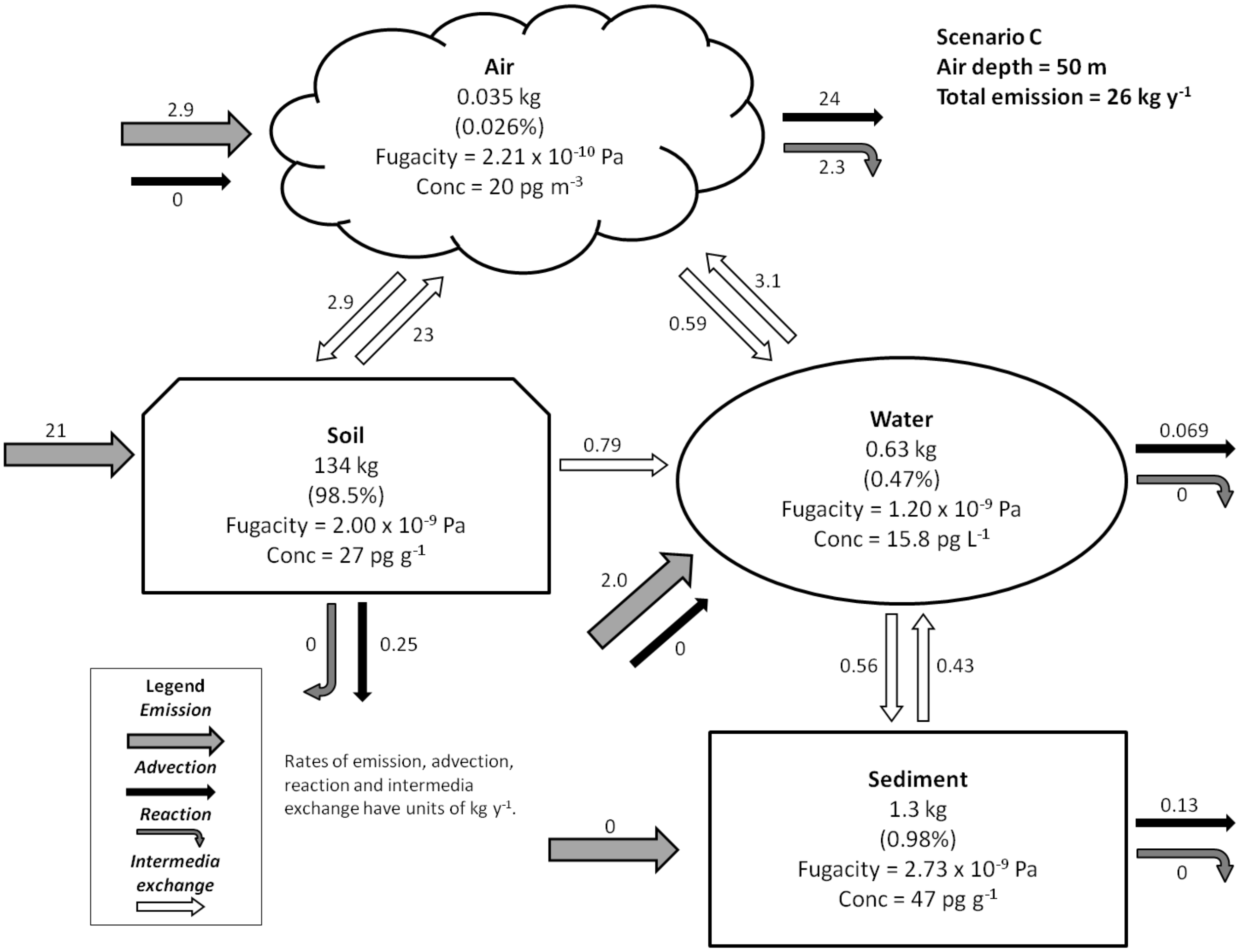
Scenario A
Air depth = 50 m
Total emission = 8.0 kg y^{-1}

Rates of emission, advection, reaction and intermedia exchange have units of kg y^{-1}.



Scenario B
Air depth = 500 m
Total emission = 78 kg y^{-1}

Rates of emission, advection, reaction and intermedia exchange have units of kg y^{-1}.



Scenario C
Air depth = 50 m
Total emission = 26 kg y^{-1}

Rates of emission, advection, reaction and intermedia exchange have units of kg y^{-1}.

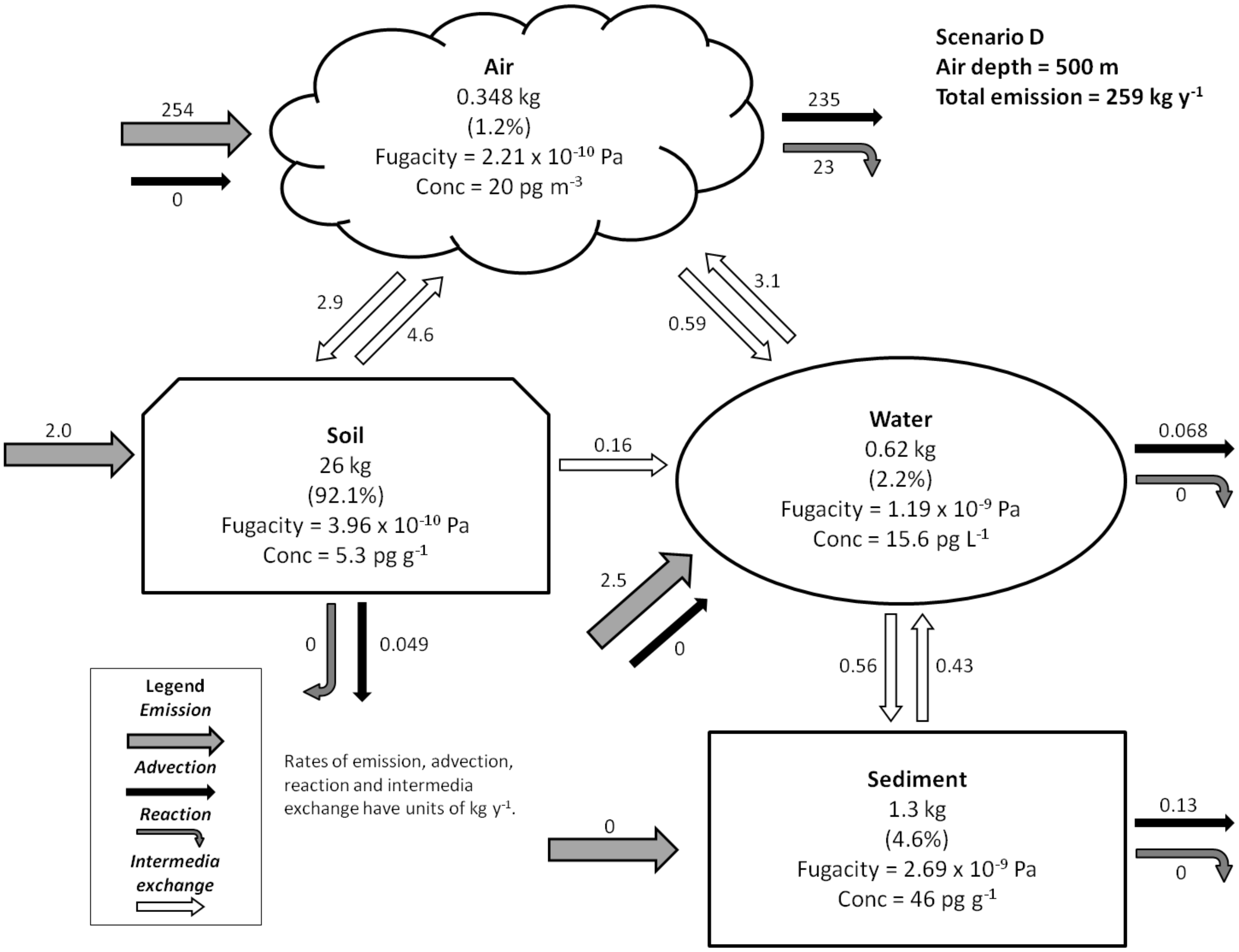


Figure S2. Distribution and mass flows of PCB 11 in the Delaware River Basin predicted by Level III fugacity model under various environmental scenarios (A-D).

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