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Inventory of PCBs in Chicago and Opportunities for Reduction in Airborne Emissions and Human Exposure

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Abstract

Urban areas are important regional sources of airborne polychlorinated biphenyls (PCBs) and population-scale airborne exposure, yet a comprehensive bottom-up source inventory of PCB emissions has never been quantified at urban scales in the United States. Here we report a comprehensive parcel level inventory of PCB stocks and emissions for Chicago, Illinois, developed with a transferable method from publicly available data. Chicago's legacy stocks hold 276 ±147 tonnes ΣPCBs, with 0.2 tonnes added annually. Transformers and building sealants represent the largest legacy categories at 250 and 20 tonnes, respectively. From these stocks, annual emissions rates of 203 kg for ΣPCBs and 3 kg for PCB 11 explain observed concentrations in Chicago air. Sewage sludge drying contributes 25% to emissions, soils 31%, and transformers 21%. Known contaminated sites account for <1% of stocks and 17% of emissions to air. Paint is responsible for 0.00001% of stocks but up to 7% of ΣPCBs emissions. Stocks and emissions are highly concentrated and not correlated with population density or demographics at the neighborhood scale. Results suggest that strategies to further reduce exposure and ecosystem deposition must focus on the largest emissions sources rather than the most contaminated sites or the largest closed source legacy stocks.

GRAPHICAL TOC

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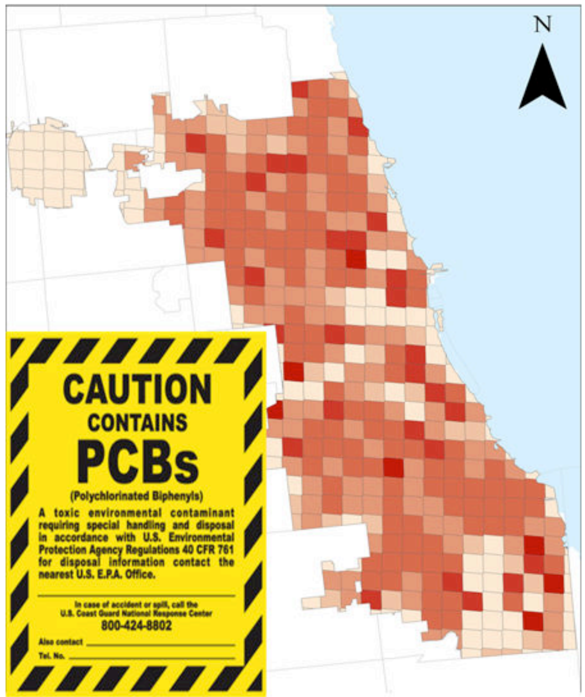

Keywords

polychlorinated biphenyls; semi-volatile organic compounds; policy; remediation

INTRODUCTION.

Polychlorinated biphenyls (PCBs) are a class of compounds that were widely used in a variety of industrial and manufacturing applications between 1929 and 1979. The Aroclor mixtures produced by Monsanto comprised the largest share of total PCB production and were common additives in dielectric fluids in electrical transformers and capacitors. Other formulations were also used as components of caulk and joint sealers, electrical wiring coatings, carbonless copy paper, and adhesives. [1,2] PCBs are classified as persistent environmental pollutants because of their resistance to chemical, thermal, and biological degradation coupled with their potential human health effects. They were initially banned because of their carcinogenicity; more recent studies have found that PCBs may also pose a threat to human neurological and endocrine systems.[3,45–7]

Airborne PCBs pose a hazard to ecosystems and humans. Although PCBs have not been intentionally produced in the US since the late 1970s, they continue to be detected in ambient air samples throughout the world. In 2000, deposition of airborne PCBs was identified as the largest categorical source to Lake Michigan[8]. PCBs are a primary cause for fish consumption advisories in the Great Lakes, fish consumption is an important dietary source of PCBs for some Great Lakes sub-populations, and recent studies have shown that inhalation of airborne PCBs is an important exposure route for children and adults.[9–12]

Pollutant source inventories are useful for quantifying emissions and exposure at local to regional scales. Source-resolving, spatially specific emission inventories are developed using a “bottom-up” approach that combines estimates of chemical production, use, and disposal with emission factors for each compound and activity.[13, 14] For criteria air pollutants, these source- centric inventories serve as the basis for atmospheric chemical transport modeling applications in air quality forecasting and regulatory decision support.[15,16] Developing and applying similar inventories for PCBs and other semi-volatile organic pollutants (SVOCs) has been limited due to uncertain and limited stock and emissions activity data, sparse concentration and emissions factors, and limited requirements for the use of atmospheric modeling in regulatory activities.

Studies to date have attempted to quantify urban PCB sources and emissions rates, primarily through “top-down” inversion of atmospheric concentration measurements, which estimate totals of stocks and emissions at urban scales but cannot resolve the contributions from each individual local source. Inventories for Zurich, Switzerland were developed using field measurements[17] and subsequently augmented with a multicompartment box model,[18,19] estimating urban emissions totals for 46 and 6 PCB congeners, respectively. A study in the New York City metropolitan area identified a local point source through observations and dispersion modeling, and extrapolated the source strength to estimate total urban emissions.[20] A series of studies in Toronto, Canada have developed bottom-up inventories for PCBs in electrical equipment and building sealants, and employed spatially specific top-down emissions estimates to simulate PCB chemical transport in multicompartment models and contextualize the potential effectiveness of Canada’s implementation of the Stockholm Convention for equipment that contains PCBs.[21–24] The Toronto inventory found that closed sources of PCBs accounted for 97% of stocks, and that emissions accounted for 0.01–0.30% of stocks, explaining observed stabilization of atmospheric PCB concentrations.

The goal of this study is to compile a comprehensive urban inventory of PCB stocks and atmospheric emissions for Chicago, Illinois. Meat packing plants, steel and iron mills, oil refineries, chemical plants, and other industries dominated the local economy in the 20th century and left a legacy of pollution, including PCBs. Like many American cities, Chicago experienced a significant building boom during the 1950s-1970s, when PCBs were commonly used in building construction and infrastructure expansion. This history, along with the city’s size, has resulted in a multitude of potential source sectors. Additionally, many reports document elevated concentrations of airborne PCBs in Chicago.[25–29] Chicago waterways are also contaminated with PCBs.[30, 31] Atmospheric PCBs in Chicago air are known to originate from multiple sources, some of which are not declining, suggesting that both fresh emissions and legacy sources contribute to observed concentrations.[32]

We developed estimates for both legacy PCB stocks contained in building sealants, known transformers, and soils, as well as variable emissions sources such as wastewater treatment plant sludge drying facilities, architectural paint, and landfills by synthesizing information from current scientific literature and publicly available databases. Developing estimates for both stocks and emissions supports an integrated approach to developing exposure assessments and policy recommendations based not only on the estimated size of each category of stock, but also its availability for atmospheric release. Building a complete, easily replicable, spatially specific, bottom-up inventory of PCB stocks from publicly available data sources is an important first step in identifying key sources of emissions and exposures to inform scientific and regulatory efforts nationally, and throughout the world.

By quantifying source stock profiles with all 209 PCB congeners, defined by number of chlorine atoms and their functional positions, this method supports assessment of the contribution of non- Aroclor PCB sources to total emissions and concentrations. It has been shown that 3,3'- dichlorobiphenyl (PCB 11) is the 5th most prevalent congener in Chicago air throughout the city. [28] PCB 11, along with more than 50 other congeners, has been identified as an inadvertent and largely unregulated by-product of diarylide, azo, and pthalocyanine pigment production.[28, 33, 34] These pigments are used in architectural paint as well as a wide range of consumer products such as newspapers and magazines, food packaging, and plastic bags. Although knowledge of the inadvertent production of PCBs during pigment production has been available to policymakers since at least the 1970s,[35] production of certain materials with PCB concentrations of up to 50 ppm produced in controlled manufacturing processes and as unintentional contaminants is exempt from the Toxic Substances Control Act (TSCA) as negligible contributors to PCB stocks and flows. This argument, however, fails to consider the fact that, while small in volume and concentration, PCBs in such applications are readily available for volatilization to the atmosphere, and also enter into the waste stream where they can contaminate recycled materials. Citywide release of PCB 11 results in an average atmospheric concentration of 24 pg m^{-3}, although the magnitude of city-wide emissions has not yet been quantified.[28]

EXPERIMENTAL/MATERIALS & METHODS

The mass of pure PCBs, their spatial distribution, and annual emissions estimates were calculated for both legacy stocks and flows from annually variable emissions sources. We included every source sector where the prevalence of materials with known PCB concentrations could be estimated from parcel-scale spatial surrogates from publicly available data.

Estimating Urban PCB Stocks

For each source sector, we estimated stocks by combining a publicly available spatial surrogate, which approximates the spatial distribution of where emissions activities take place or source materials are stored, with a reported source-specific PCB mass concentration or emissions factor. For stocks with source materials where congener-specific PCB concentration estimates were unavailable, they were calculated from the profiles of Aroclor mixtures used in those applications, using reported fractional contributions of each PCB congener to the Aroclor mixtures.[36] Data for each source sector are summarized in Table 1. Unless otherwise noted, the City of Chicago 2010 Land Use Survey[37] served as the primary source for all spatial surrogates. This dataset contains parcel area; building footprint, age, and number of stories; and zoning information for each individual parcel. Chicago's parcels, or individual taxable plots of land, range in area from <0.1 hectare for residential plots to 10+ km^2 for large public parks. Thus, this inventory resolves stocks and emisisons activities at the highest spatial resolution currently possible. Here, we aggregate parcel level results to a 1.33 × 1.33 km^2 Lambert Conformal Conic grid to identify variability at the neighborhood/census tract scale that an urban chemical transport modeling system would resolve. All GIS processing was conducted using ArcGIS 10.1. For each stock category, we estimated net uncertainty ranges by propagating known sources of variability in PCB concentrations and activity estimates.

Legacy Stocks—We define legacy stocks as sources generated during the initial period of PCB production that have not yet been eliminated.. This category includes polysulfide sealants in buildings constructed between 1940 and 1979, transformers documented in the National Transformer Registry, soils, and known contaminated sites including the Chicago Confined Disposal Facility and the Chicago Sanitary and Ship Canal.

Sealants—Building sealants are an important PCB reservoir in Chicago. During their period of production, PCBs were added to caulks and joint sealants as a plasticizing agent that also improved product durability. [1] In buildings constructed or renovated before 1977, such products were used to seal joints between masonry units and around windows. Previous studies have reported total PCB concentrations up to 33,000 ppm in caulking/gasket materials, foamboard insulation, and HVAC system parts. [38] We calculated the volume of all Chicago buildings constructed between 1940 and 1979 from building footprint and height data. Employing the methodology, conversion factors, and average PCB concentrations established by Diamond et al. (2010) [21] and Robson et al. (2010) [24], we combined building volume, average mass of sealants per unit volume (55 g m^{-3}), and average sealant PCB concentration (0.00463 g/g). Without local information on the prevalence of PCB in buidling sealants, we applied an identical estimate that 14% of buildings constructed from 1940–1979 contained PCB sealants. We propagated uncertainties using the range of PCB concentrations reported by Robson et al. Building sealants used during the target time period were primarily formulated using Aroclor 1254.[3]

Transformers—Insulating fluids used in electrical transformers and capacitors represented 75% of total PCB sales in the United States. [1] However, only 5–10% of all the transformers manufactured during the era of PCB production actually contained PCBs due to the availability of less expensive alternatives. [1] By mass, the majority of PCBs in these applications were used in transformer askarel, with a single transformer containing 200 – 2,000 kg of insulating fluid. [1] Data on known transformers stored in the Chicago area came from the 2011 National Transformer Registry, which documents 177 registered transformers in the area. [39] In addition to transformers listed on the voluntary national registry, Hsu et al. (2003) documented a large transformer storage yard located at the intersection of First Ave and the Eisenhower Expressway, and estimated that the acre lot could potentially contain up to 500 PCB-containing transformers. [29] The mass of PCBs contained in stored electrical transformers was calculated using methods previously applied to Toronto. [21] Mass was estimated for registry entries with incomplete data, as well transformers located at the unregistered storage yard noted by Hsu et al., by determining average transformer weight based on complete registry entries listing the number and weight of transformers stored in the Chicago area. We applied prior estimates that insulating fluids accounted for approximately 30% of a transformer's total mass and contained 60% PCB composition

(80% maximum, 40% minimum)[21]. Erickson & Kaley (2010) catalogued the use of Aroclors 1242, 1016, 1254, and 1260 in the dielectric fluid of transformers and capacitors. [1] Leakage rates of 0.06% $year^{-1}$, based on studies from the 1990s,[40] were bounded by an order of magnitude to reflect uncertainty in contemporary leakage under unknown storage and use conditions.

Soils—Soil may be one of the largest global PCB repositories, potentially containing 21,000 tonnes of PCBs worldwide due to deposition from manufacturing, leaching from building materials or landfills, and the application of wastewater treatment plant biosolids. [41] We estimated the volume of soil in contact with the atmosphere by synthesizing zoning classification information from the 2014 City of Chicago Zoning and Land Use Ordinance with estimates of the fraction of pervious surface associated with urban land uses, assuming a soil:air exchange depth of $^{0.1212}$ m. [22, 42, 43] The concentration range for PCBs in urban soils (3 – 220 ng/g dry weight) was estimated from 15 cities globally (averaging 50 ng/g), and the range of total PCB mass estimated using the average bulk density of urban soils. [42, 44] We estimated 50% (10% - 100%) of all pervious surfaces as urban soils to account for variability in exchange depth, density, and estimates of pervious surface fraction for each urban land use type. We did not account for the potential impact of vegetation on emissions rates from soils.

Contaminated Sites—Two contaminated sites in Chicago are known to contain sediments with high PCB concentrations. The Chicago Sanitary & Ship Canal (CSSC) opened in 1900 to carry shipping traffic and reduce the amount of pollution flowing into the Lake Michigan drinking water supply via the Chicago River. Medium and heavy industrial firms were primary users of the canal during Chicago's "Golden Age" of industrial development (1895–1920), when "many business owners…perceived the canal as an 'open sewer". [45] The CSSC extends 53.1 km from Chicago to Lockport, IL, and receives discharge from the Stickney and Lemont Water Reclamation Plants (WRPs). [46–48] CSSC sediment volume was calculated from the average width of the canal (62 m) and an estimated sediment depth of approximately 0.1 m. Speciated PCBs concentrations in CSSC sediment were taken from a 2006 sediment quality study by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC), and we assumed no reduction in sediment PCB concentration from 2006 to 2011. Sample concentrations for Aroclors 1016, 1248, 1254, and 1260 mapped to a profile of 209 congeners measured in the Indiana Harbor and Ship Canal (IHSC). [31, 49] Given the similarity in historical and contemporary land use (steel manufacturing, petroleum refineries, heavy industry) and Aroclor applications, the PCB congener profile of CSSC sediment appears similar to that of the IHSC in nearby East Chicago, Indiana, with both dominated by Aroclor 1248.

The Chicago Area Confined Disposal Facility (CDF) is an Army Corps of Engineers facility constructed in 1984 south of Calumet Harbor to store contaminated sediment dredged from the Calumet River and the Chicago River/Harbor. [50, 51] The mass of pure PCBs contained in the CDF was calculated from the CDF's estimated soil volume, soil density, and the average PCB concentration of contaminated sediments (0.0025 mg/g), and emissions estimated from exposed surface area. [29] We applied the IHSC congener profile to the CDF sediment, including the presence of Aroclors 1248, 1254, and 1260. In the absence of congener-specific sample analyses, we estimated profiles from these sources only for Aroclors, and excluded any potential presence of non-Aroclor PCBs.

Variable inputs to PCB stocks and emissions—PCB use, processing, recycling, and new production within the urban system result in both material flows and emissions into the atmosphere. The inflows of PCBs into urban stocks and the emissions the air from these non-legacy sources fluctuate from year to year. Sources in this category include sewage sludge drying beds at municipal wastewater treatment plants, landfills, and architectural paint.

Sludge drying—Sewage sludge drying beds at municipal wastewater treatment plants are a documented source of PCBs. [29, 52, 53] The MWRDGC is served by seven WRPs. Sewage sludge collected during the water treatment process is dried and, depending on quality, used as fill in recreation areas, final landfill cover, and other landscaping projects as part of the district's biosolids program. [54] Biosolids are also applied to farmland in a semi-dried state or simply disposed of in municipal landfills. The mass of PCBs in sludge generated annually at MWRDGC facilities was calculated from the mass of biosolids produced district wide (170,462 tonnes) and the average concentration of ΣPCBs in municipal sewage sludge (1.0 mg/kg dry weight). [1132] Three of MWRDGC's biosolids-producing wastewater treatment facilities were included in our estimate due to their proximity to the City of Chicago, including the Stickney WRP, the district's largest sludge producer, located along the Chicago Sanitary and Ship Canal at the western boundary of the city. The Calumet (southeast) and Terrence J. O'Brien (northeast) WRPs were also included. We assume that biosolids produced at Chicago's WRPs exhibit a congener profile similar to the human PCB body burden and the wastewater profile. [55, 56] We allocated stocks and emisisons to the three WRPs by the reported areas of their sludge drying beds.

Landfills—Without local source data, the total stock of PCBs in Chicago landfills is unknown. However, the emissions to air from PCBs in landfills can be estimated. Municipal landfill gas contains PCB concentrations of up to 400 ng m^{-3} [57] and a Chicago landfill was found to emit 239 μg s^{-1} [29], and possibly higher for facilities that accept hazardous materials. PCBs were used in a multitude of landfilled products, including carbonless copy paper, small capacitors in consumer electronics and appliances, and construction and demolition materials.[1, 58] While unquantified at local scales, these stocks of legacy PCBS from demolished buildings and electrical equipment were typically disposed of in local landfills rather than incinerated or treated as specialized hazardous waste. Landfills also contain PCBs from products currently in production, such as leftover architectural paint, pigment-containing packaging and print materials, and biosolids as both waste and fill material. [31, 34, 41] Lacking data on landfill materials, volumes, dates, and PCB concentrations, we did not develop an estimate for the mass of PCBs contained in Chicago landfills. Three landfills have been constructed within Chicago city limits since 1967: CID RDF #3 (closed 2009), Harbor View Landfill (closed 1998), and River Bend Prairie Landfill (the single active landfill in Cook County). The congener profile of a landfill reflects the profiles of its composite materials. Murphy et al. (1985) noted the presence of PCB-containing carbonless copy paper and capacitors from consumer white goods in older landfills; these items are known to contain Aroclor 1242 and Aroclors 1242, 1016, and 1254, respectively.

Paints & Pigments—Architectural paint has been identified as a source of airborne PCB congeners unrelated to historical use of Aroclors. These congeners are present in paint due to inadvertent production during the manufacture of pigments. The US EPA documented the presence of PCBs in dried paint at concentrations ranging from <1 ppm to 97,000 ppm (0.001 to 97 ng/g) [59]; Hu & Hornbuckle (2009) detected PCB concentrations in commercial paint pigments ranging from 2 to 200 ng/g fresh weight. [33] Pigments used in paint, packing materials, and other consumer products are currently the only known sources of PCB 11.

We estimated the stock of pure PCBs from in-use architectural paint, and used annual volume of paints sold by Chicago retailers to estimate the inflow of new paint added annually. The spatial distribution and total stock of in-use architectural paint was approximated using building interior wall area as a spatial surrogate, estimated from building footprint and number of stories. To estimate the volume of paint sold in the Chicago area each year we began with national paint/architectural coating sales. [60] Using Chicago-specific data on sales and production values from the 2007 Economic Census, we estimated the volume of paint sold and produced locally each year, and further refined this estimate to reflect the estimated market share of PCB- containing organic pigments (30%). [61, 62] We then estimated the mass of pure PCBs added to Chicago buildings via annual retail sales and annual production from sales and production volumes, paint density, and the average congener-specific PCB concentration of whole paint. The Chicago area's 20+ paint manufacturing operations may also be a potential point source of PCB emissions, but stack emissions rates due to production have yet to be quantified. There are over 50 PCB congeners in commercial paint pigments and the specific congeners present varies among pigment types and manufacturers. [33] We applied an average profile for ΣPCBs based on sales volume and color for paints with PCB-containing dyes, highlighting results for PCB 11, the most commonly detected non-Aroclor congener. We assumed all paint emitted indoors makes it way to outdoor air without loss.

The Human Reservoir—Human body burdens provide a natural for contextualizing the magnitude of PCB sources in the urban environment, and may represent a primary source of PCBs to municipal wastewater. We estimated PCBs in Chicago residents and direct emissions from respiration using ACC-HUMAN, assuming steady state body burdens and configuring ACC-HUMAN with observed Chicago air and water concentrations and U.S. dietary PCB consumption. [63, 64]

Emissions Modeling

We calculated annual emissions rates from the mass of pure PCBs for each source sector on the km grid. We estimated annual emissions rates by integrating hourly congener-specific fugacity-based gas phase mass transfer, following the steady-state approach of Diamond (2001) for soil:air, water:air, and film:air exchange.[21, 65. 21, 23] Mass transfer coefficients were calculated from hourly quality-controlled observations of temperature, pressure, and wind speed at Chicago O'Hare Airport from the NOAA Quality Controlled Local Climatological Data. As water temperature monitoring in the CSSC began in 2015, CSSC water temperature was estimated from U.S. Geological Survey 2013–2014 hourly observations of the Des Plaines River at Channahon, Illinois, the nearest available site, and the river to which the CSSC drains.[66] We propagated through all emissions rates the 7% uncertainty attributed the use of the single O'Hare observational site to represent variability in urban meteorology across Chicago on the 1.33 km grid.[67]

RESULTS AND DISCUSSION

Chicago PCB stock inventory

The total mass of ΣPCBs stored in legacy stocks (sealants, transformers, soils, the CDF, and the CSSC) is approximately 276 (121 – 414) tonnes. Transformers and sealants represent the largest stocks, and contain 250 and 20 tonnes of ΣPCBs, respectively. Areas with a greater number of buildings constructed between 1940 and 1979 are expected to contain larger amounts of PCBs associated with building sealants. These include residential districts along the north and southwest edges of the city, which expanded rapidly after World War II, as well as the dense landscape of skyscrapers downtown. Other "hotspots" align with the locations of large transformers and transformer storage facilities, as in southeast Chicago, a historically industrial area that now houses a cluster of transformer warehouses. [68] Variable inflows (paint and WRP sludge drying beds) make only a small annual contribution relative to the total stock, adding an estimated 0.2 tonnes each year, with paint adding only 0.00001% to the existing stock each year.

Chicago Emissions Rates & Atmospheric Concentrations

We estimate annual PCB emissions from all quantified sources as 203 (94–736) kg year^{--1} (Table 2). Approximately 70% of this total is attributable to volatilization from legacy sources, while the remaining 30% is released from variable sources. Municipal sludge drying beds represent roughly 25% of total annual emissions, a significant portion considering their small contribution to total stocks. Similarly, although paint increases Chicago's total PCB stock by only 0.00001% each year, it accounts for 1.7% (0.2% - 6%) of total annual ΣPCB emissions and all primary PCB11 emissions accounted for in this inventory. Depending on soil concentrations and transformer leakage rates, we also expect 30% of total annual emissions to come from soil, and an additional 22% from transformers. The body burdens of Chicago residents total to 58 kg, and account for flows of 18 kg/year to wastewater, with the remaining PCBs in biosolids due to industrial sources and suburban populations served by the MWRDGC.

The spatial distribution of annual emissions (Figure 2a) mirrors that of total PCB stocks (Figure 1b), with hotspots near known transformer storage locations (Figure 1a). Emissions from soils are concentrated in single-family residential districts and other areas with higher proportions of pervious surface cover (Figure 2a). The majority of biosolids production in the Chicago area takes place at the Stickney Water Treatment Plant in Cicero, just west of the Chicago city limits. Emissions are highly concentrated, as shown in maps of ΣPCB and PCB 11 emissions on semilog scales in Figure 2. The 98th percentile (top 10) and 88th

percetile (top 50) of gridcells with the highest PCB levels are responsible for the majority of the city's ΣPCB stocks (64%, 81%) and emissions (52%, 75%). These concentrated locations are often the same for legacy and non- Aroclor emissions: the top 10 grid cells for PCB11 emissions contain 5 times more ΣPCBs and almost 7 times more ΣPCB emissions than the average populated grid cell.

We estimated atmospheric concentrations using an inert tracer box model over the city (588 km^2, 450 m mixed layer, Chicago O'Hare airport observed average wind speed of 4.2 m s^{-1}). Average concentrations due to this inventory would be 1.26 ng m^{-3} for ΣPCBs and 19.03 pg m^{-} for PCB 11,roughly matching observed ambient concentrations in the city of 1.13 ng m^{-3} and 24 pg m^{-3}, respectively. [25, 27, 69]

Comparison to other stock and emissions inventories

We compare results to prior inventories, urban source identification efforts, and emissions estimates in order to contextualize results from this study, confirm findings from prior studies, and improve understanding of urban PCBs.

One key question about PCBs from the urban environment is the degree to which population- based estimates, developed for use in global chemical transport studies, can predict the magnitudes and distributions of PCB sources and emissions at the spatial scales needed for urban and regional policy assessment. To produce a population-based estimate at the local scale following the methods of Breivik et al. (2001), we allocated their estimate of total historic PCB consumption to the 2010 US population, yielding a national estimate of ΣPCB mass per capita. [70] This value was then applied to the city of Chicago, resulting in a citywide top-down ΣPCB stock estimate of 2200 tonnes (Table 3), an order of magnitude greater than this study's bottom- up estimate. A national, production-based approach represents a maximum estimate for all PCBs since their initial introduction to the market, while our estimate represents the current stock that can be accounted for from known sources. However, even an inventory based on all-time integrated use and disposal may be biased low due to the extensive use of PCBs in manufacturing in Chicago and PCB transport through the city by rail, which could lead to stocks far exceeding the expected local footprint.

Our inventory for Chicago is consistent with estimates of stocks and emissions for Toronto (Table 3), a city of similar age, geographic area, total population, and population density. Toronto's known transformer stock inventory is higher, with overlapping uncertainties. As a fraction of total stocks, the resultant net emission rate estimate of 0.1% (0.07% - 0.18%) is consistent with prior urban modeling for PCBs (0.01%−0.3%) and ΣPBDEs (0.01%) in Toronto. [21,23, 71] Our inventory is roughly 14 times greater than the emissions estimate for Zurich, Switzerland, based on inversion of PCB concentrations in air.[17, 18] While Zurich and Chicago have similar population densities, Zurich has roughly 15% of Chicago's population and land area, and its less extensive industrial history likely explains why it has only half the ΣPCB emissions on a per-capita basis.

Results for Chicago corroborate that transformers and building sealants are the most important urban stocks, but that an inventory based exclusively on mass excludes the majority of key contributors to urban emissions. Instead, the Chicago inventory underscores the realization that urban PCB concentrations arise due to multiple distinct point and area source sectors requiring different remediation strategies. [72] An independent source apportionment study of observed concentration profiles in Chicago suggested 17–20% of ΣPCBs are due to leaks from closed sources, 17–20% from dispersed Aroclors, and 21–22% from secondary sources—contributions that align closely with this study's central estimates of transformers (21%) as closed sources, dispersed Aroclors from sealants and contaminated sites (18%), and soils (34%) as a dominant secondary source.

Emissions estimates are contextualized by an inventory of reported emissions for the Great Lakes region, which found volatization from the lakes to air of 29 tonnes from 1992–2000.[40] While the reported values likely underestimate total releases, they highlight the importance of emissions from Chicago to the regional budget: quantified annual emissions from Chicago correspond to 6.2% (2.8% - 20.8%) of the reported decadal release of PCBs to air across the 244,000 km^2 surface area of the lakes, and represent observed enhancement of PCB 11 in samples throughout the lower Great Lakes.[73] Emissions rates are also consistent with prior studies, considering population and economic and land use histories, with prior estimates for Milwaukee (120 kg $year^{-1}$) and New York City (300 kg $year^{-1}$).[20,74] Overall, considering annual deposition of 1500 kg $year^{-1}$ to Lake Michigan[75] and observed atmospheric concentrations in the city, this inventory likely resolves most emissions from the City of Chicago, especially if its suburbs and the lake's industrialized southern shore are each responsible for similar quantities.

Exposure demographics

We compared PCB stocks and emissions to U.S. Census 2010 tract-level demographics on the km modeling grid to determine whether any groups face an inordinately high exposure risk from living in close proximity to PCBs. Demographic characteristics included race, median household income, disability status, as well as populations under 18 or over 65 years of age. Total population density was correlated with PCB 11 emissions (r^2 = 0.55) but not with £PCB stocks (r^2 = 0.003) or emissions (r^2 = 0.004). Density is strongly correlated at this spatial scale with poverty (r^2 =0.994), children, and the disabled. No statistically significant correlations were found with any demographic group's population or local prevalence after accounting for population density. Thus, on a city-wide basis, all demographic groups have a similar risk of exposure to stocks and emissions from this inventory. However, city level comparisons have limited applicability to PCBs, as stocks and emissons are concentrated in industrial districts with low populations. We therefore assessed the populations living near the top 10 and top 50 gridcells with the highest PCB levels, as compared to the citywide average, and applied a similar analysis to the 98^{th} and 88^{th} percentiles for each demographic variable (SI). We found few environmental justice issues related to local PCB sources at the 1.33 km scale. Areas with the highest ΣPCBs (both emissions and stocks) and PCB11 emissions were generally more dense than the average gridcell, with fewer children, senior citizens, and disabled persons than average. PCB11 emissions hotspots are associated with both diverse and segregrated residential areas: with both higher household incomes and more people in poverty, and higher proportions of white, Latino, and Asian-American residents. Neighborhoods with the highest concentrations of senior citizens and Caucasians contained nearly twice as many PCB stocks and emissions than average.

Uncertainty in Stock and Emissions Estimates

These estimates are subject to large uncertainties in the source sectors included, the representativeness and accuracy of PCB concentrations in each material, the completeness of the spatial surrogates in representing the current presence and emissions of PCBs, and the emissions modeling. Among nine source categories, building sealant and soil concentrations are the only parameters for which global observations support the estimation of a probability distribution, and may not be representative for Chicago.

We identify transformers quantities, PCB concentrations, and leakage rates as the most important net uncertainties in the inventory, followed by soil concentrations and their correlations with urban land use classifications. Transformer leakage rates have not been re-examined since the 1990s, and likely represent the greatest quantifiable source of parametric uncertainty, with our order of magnitude bounding of leakage rates responsible for up to 90% of uncertainty in the stock inventory and 71% of emissions. The representativeness of PCB concentrations and their congener profiles for urban soils are the only other major source of parametric uncertainty (26%) in the emissions inventory, and currently omit the much higher concentrations possible at former industrial sites, along railroads, and in residential areas that were once downwind of large point sources. Other sources omitted from this inventory are likely a far greater source of uncertainty. The voluntary nature of the National Transformer Registry and documented presence of unregistered transformers in storage in Chicago suggests a potentially higher contribution from this large sector. Manufacturing and industrial processes known to inadvertently emit PCBs are associated with cement kilns, titanium processing, and steel mills, and are likely the largest unresolved contributor to emissions.[76]

Unresolved contributions from other closed sources (e.g. light ballasts) are likely of the same magnitude as sealants, and feature the same poorly quantified leakage rates as transformers, but are even more difficult to enumerate. Given their potential importance as sources to indoor concentrations and exposures and the relatively low cost of removal and replacement, policies to control light ballasts and other in-use closed sources may represent a tractable incremental step for reducing indoor exposures, independent of their unquantified contributions to PCB stocks, emissions, and outdoor concentrations. Despite the potential for widespread and diffuse use and distribution of PCB 11 sources, we focused solely on architectural paint to approximate the size of potential PCB 11 sources in Chicago. We expect pigments in paper, receipts, clothing, furniture, building materials, and other consumer products to make negligible contributions to total stocks, and small but important sources to outdoor and indoor air.

Policy implications

Results from this study have large policy implications in refocusing efforts to reduce urban PCB concentrations and population exposures in the U.S. and in urban areas globally. To date, U.S. efforts to reduce PCBs in humans and the environment (e.g. the Toxic Substances

Control Act and the Comprehensive Environmental Response, Compensation, and Liability Act) have focused on eliminating new sources of PCBs and remediating major Aroclor sources such as electrical equipment and highly contaminated sites. However, we find that secondary sources are responsible for more than 67% of emissions. Though open applications of PCBs were officially banned in 1973, diffuse and/or inadvertent sources are not regulated as long as they comply with monitoring/reporting requirements. [34] Emissions from open, easily volatilized secondary sources contribute significantly to observed ambient PCB concentrations in urban air; the fact that there are no reporting PCB emitters in Chicago in the most recent (2013) Toxic Release Inventory suggests that such sources may indeed warrant renewed regulatory interest.

Current policies such as CERCLA (1980), the Great Lakes Binational Toxics Strategy (1997) EPA's Region 5 Polychlorinated Biphenyl Phasedown Program (1999), and the Great Lakes Restoration Initiative (2011) have emphasized reducing the largest stocks and most contaminated sites, with the assumption that these most concentrated stocks are the a greatest threat, rather than specifically quantifying and systematically reducing total human or ecosystem exposure or harm. As a result, limited reductions in ambient concentrations and urban, regional, and global atmospheric transport and deposition have remained mostly unquantified externalities. The first generations of toxic substances policies have proven to be a good starting point by eliminating many of the largest highly concentrated PCB stocks and uses of legacy Aroclors, such that contaminated sites represent a small fraction (17%) of the emissions inventory for a large postindustrial urban area, and there are no regulated uses or emissions of Aroclors in the city. However, such incremental policies do not provide a comprehensive, rational planning framework for managing all PCB emissions from dispersed sources. Our findings suggest that alternative courses of action that take into account source availability as well as size may be necessary to achieve additional reductions in atmospheric PCB concentrations. This marks the beginning of a new phase in a natural progression: the success of policies like CERCLA and TSCA in halting the production of highly concentrated PCB materials and remediating contaminated sites means that the most important sources of PCBs to the environment are now smaller, more widely dispersed, and due more to inadvertent manufacturing byproducts, building materials, contaminated soils and sediments, and biota than to legacy supplies in closed sources.

Even in this context, the largest PCB reservoirs are not necessarily the largest contributors to air concentrations or exposures. This work emphasizes the importance of distinguishing between the mass of PCBs contained in a source and the stock's availability for volatilization. When deciding on a course of action, efforts to reduce airborne PCBs and PCB deposition to ecosystems should take emissions potential into consideration, rather than mass alone. This is especially true for variable sources, which can play a significant role in contemporary urban PCB emissions despite their small contributions to the total stock. While such sources have not typically been included in urban source inventories, we find that they make significant contributions to atmospheric PCB concentrations, greater than the average estimate for annual emissions from transformers. PCB 11 is one of the most volatile PCBs and may be emitted to air within hours to days of paint application. This congener has been consistently detected in ambient air samples, and there are no known sources other than paints and pigments. The preliminary results of this study suggest that despite paint's relatively small contribution to the total stock, emissions rates are consistent with observed atmospheric concentrations of PCB 11. [28] The contribution of paint should therefore be further investigated to assess the potential need for regulatory action. This includes in-use architectural paint, which could present significant indoor exposure risks, as well as emissions from paint and pigment manufacturing facilities, which may be potentially significant PCB point sources.

Initiatives to reduce PCB emissions associated with WRP sewage sludge drying facilities would address a major source of PCBs to the air while providing additional benefits. Fly ash has been shown to effectively and inexpensively remove PCBs and other organic compounds from wastewater and biosolids. [77] Affordable PCB-eliminating phytoremediation using poplars[78], grasses[79], and wetlands plants [80] or bioremediation using transgenic bacteria may also reduce the levels of other potentially harmful compounds that have been detected in municipal wastewater and biosolids and in Lake Michigan, including persistent organic pollutants, medications, hormones, and personal care products. [81–84] Such improvements in the wastewater treatment process may also preclude regulatory action under the Federal Clean Water Act, which regulates PCB levels in waterways where a Total Maximum Daily Load (TMDL) for PCBs has been established.

Financial incentives for program compliance have not significantly decreased PCB stocks in the U.S. or Europe. In the U.S., states and tribes are eligible to receive funding to support compliance through TSCA’s Compliance Monitoring Cooperative Agreements. However, out of 77 total grants in FY2013, only 7 went to PCB projects, and even those were for tasks such as conducting inspections rather than actually removing or destroying PCBs.[85] Despite employing a different approach, Belgium and the Netherlands both experienced only minimal success via programs to provide subsidies for private companies to upgrade equipment containing PCBs.[86] These examples suggest that financial incentives may not be effective in making significant reductions in legacy stocks.

The US and other industrialized nations have experienced similar challenges in reducing ambient PCB concentrations. Building and maintaining complete and accurate inventories has been a major difficulty globally, as have data gaps created by the absence of comprehensive data on environmental PCB concentrations and the challenges of comprehensively quantifying sources.[86] This study highlights the potential global benefit from looking beyond large, traditional sources in identifying and reducing the inadvertent production and emission of PCBs. The 50 ppm internationally accepted benchmark concentration may have been beneficial in the initial regulation of large stocks, but this target now stands to be broadened to include more volatile large volume emissions sources.

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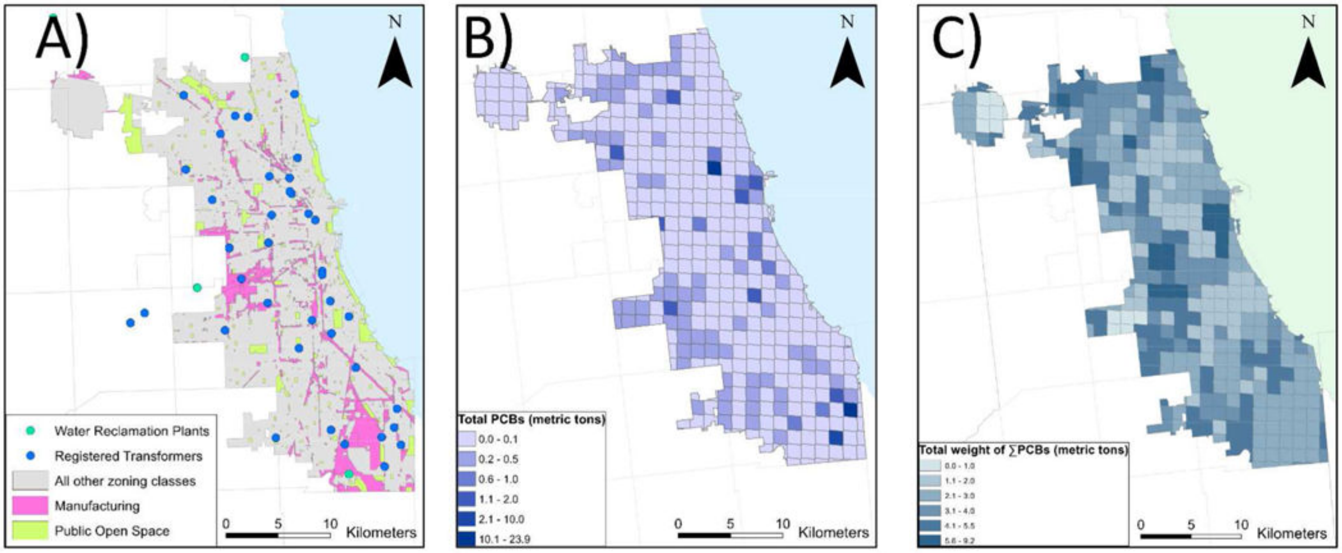

Figure 1.

PCB stock estimates and spatial surrogates: a. City of Chicago zoning for manufacturing (pink) and open space (green); Locations of PCBs point sources indicated for transformers (blue) and sludge drying facilities (teal); b. Spatial distribution of ΣPCBs contained in Chicago's PCB stocks (excluding municipal landfills); c. Chicago PCBs allocated by population, following the methods of Breivik et al. (2001).

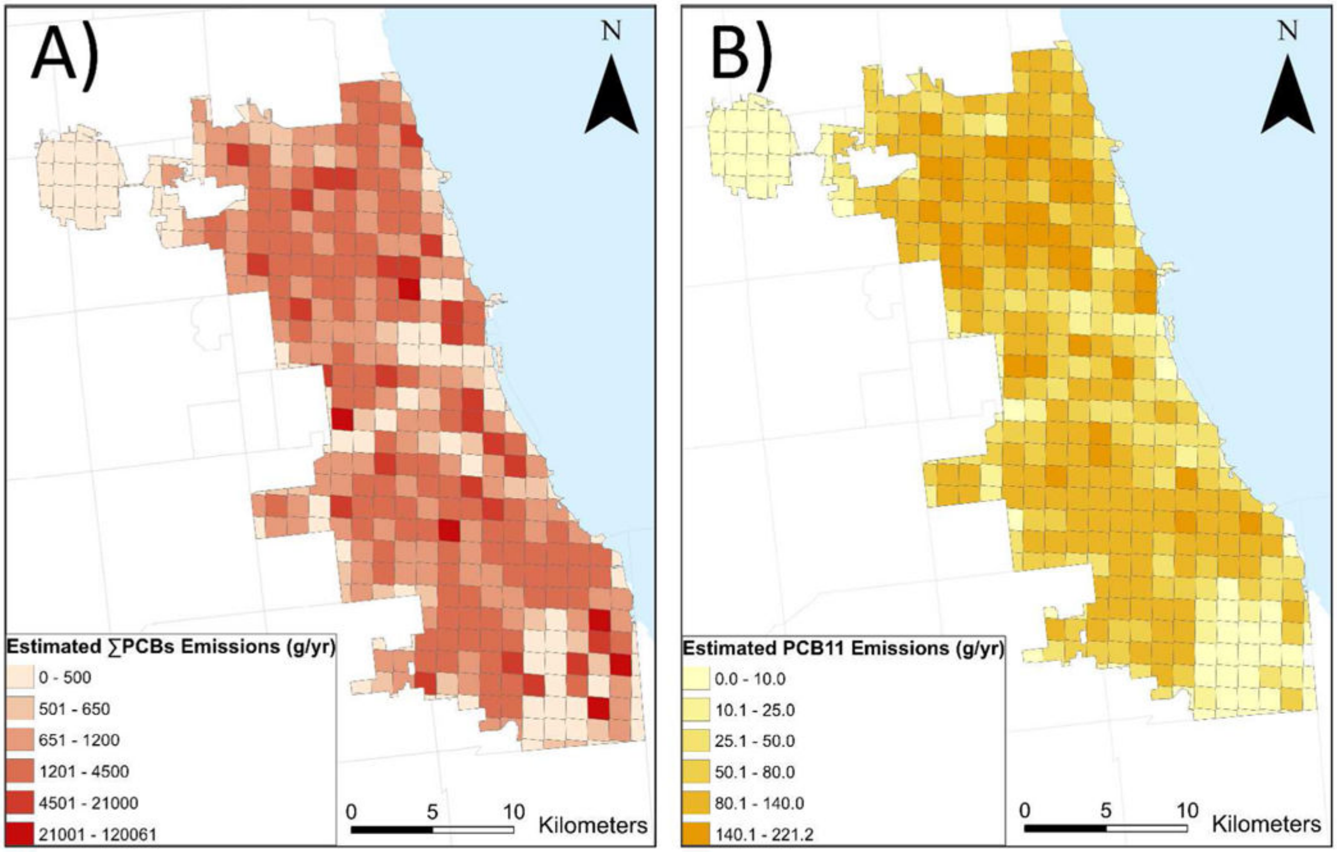

Figure 2.

Spatial distribution of estimated annual PCB emissions (g year^{-1}): a. Annual ΣPCB emissions from all sources; b. Estimated annual PCB 11 emissions from architectural paint.

Table 1.

Source sector stock and emissions parameters. spatial surrogate totals, and associated data sources

Source Sector	Spatial Surrogate	Surrogate Factor	Central ∑PCB Concentration or Emission Factor	Aroclor Profile
Sealants	Building volume	156 m^3	599.30 g m^{-3}	1254
Transformers	National Transfomer Registry locations	transformers	358,000 g m^{-3}	1242, 1016, 1254, 1260
Soils	Pervious surface area	357 km^2	0.10 g m^{-3}	Non-Aroclor
Chicago CDF	Surface area	0.17 km^2	9.00 g m^{-3}	1248, 1254, 1260
Chicago Sanitary & Ship Canal	Canal volume, sediment depth	3 km^2	Sediment: 8.3 g m^{-3} Water: 33 ng m^{-3}	1248, 1254, 1260
Paint: in use	Building wall area	79 km^2	0.0134 g m^{-3}	Non-Aroclor
Municipal landfills	Landfill area	12 km^2	0.045 μg s^{-1} m^{-2}	1242, 1016, 1254; Non-Aroclor
Sludge drying beds	Biosolids production	4 km^2	0.72 g m^{-3}	Non-Aroclor
Human population	Population density	4,450 persons/km^2	0.01 g/person	Non-Aroclor

Table 2.

City of Chicago ∑PCB mass and annual emissions estimates by source sector.

Source Sector		
Legacy stocks	**Stock of pure PCB (tonnes)**	**∑PCB emissions (kg year^{-1})**
Sealants	20	2 (2–3)
Transformers	250 (120–390)	42 (4–452)
Soils (background)	2.2 (0.02–22)	64 (6–172)
Chicago CDF	1.3	26 (24 −28)
Chicago Sanitary & Ship Canal	1.2 (0.6–1.8)	8 (4–13)
Subtotal: Legacy stocks	*276 (121–414)*	*142 (40–668)*
Variable flows		
Architectural Paint: In Use	$2 \cdot 10^{-5}$ (10^{-5} - $9 \cdot 10^{-5}$)	3 (1–6.5)
Municipal landfills	N/A	1.7 (1.3–2.3)
Human body burden	0.06	6
Sludge drying beds	0.2	50 (46–54)
Subtotal: Variable flows	*0.2*	*61 (54–69)*
Total	**276 (144–418)**	**203 (93–736)**

Table 3.

Comparison between results from this study to population-weighted emissions for Chicago calculated using the approach of Breivik et al. (2011) and prior urban estimate for Toronto, Ontario.from Diamond et al. (2010).

	Applying Breivik's (2001) methods to Chicago	**Toronto**	**This study: Chicago**
Estimated ΣPCB stock	2,200 tonnes	437 tonnes[21] *(282–796)*	276 tonnes *(144–418)*
Estimated ΣPCB emissions	--	230 kg $year^{-1}$[23] *(40–480)*	203 kg $year^{-1}$ *(93–736)*