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Room-to-Room Variability of Airborne Polychlorinated Biphenyls in Schools and the Application of Air Sampling for Targeted Source Evaluation

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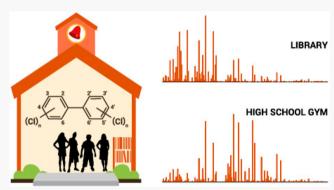
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ABSTRACT: Airborne polychlorinated biphenyl (PCB) concentrations are higher indoors than outdoors due to their historical use in building materials and their presence in modern paints and surface treatments. For some populations, including school children, PCB levels indoors result in inhalation exposures that may be greater than or equivalent to exposure through diet. In a school, PCB exposure may come from multiple sources. We hypothesized that there are both Aroclor and non-Aroclor sources within a single school and that PCB concentration and congener profiles differ among rooms within a single building. To evaluate this hypothesis and to identify potential localized sources, we measured airborne PCBs in nine rooms in a school. We found that schoolroom concentrations exceed outdoor air concentrations.



Schoolroom concentrations and congener profiles also varied from one room to another. The concentrations were highest in the math room (35.75 ng m $^{-3} \pm 8.08$) and lowest in the practice gym (1.54 ng m $^{-3} \pm 0.35$). Rooms in the oldest wing of the building, originally constructed between 1920 and 1970, had the highest concentrations. The congener distribution patterns indicate historic use of Aroclor 1254 as well as modern sources of non-Aroclor congeners associated with paint pigments and surface coatings. Our findings suggest this noninvasive source identification method presents an opportunity for targeted source testing for more cost-effective prioritization of materials remediation in schools.

KEYWORDS: polychlorinated biphenyls, atmospheric chemistry, gas chromatography mass spectrometry, positive matrix factorization, principal component analysis, Aroclor, non-Aroclor

■ INTRODUCTION

Polychlorinated biphenyls (PCBs) have been a persistent organic pollutant of our atmosphere, sediment, water, and infrastructure for decades. Mass production of Aroclors began in the 1930s and persisted in the United States until the late 1970s. Aroclors were used in many applications such as pesticides, transformers, capacitors, caulk, adhesives, printing inks, and paints. Their stability and widespread use resulted in significant environmental contamination and risk to human health. For these reasons, PCB production was banned in the Toxic Substance Control Act enacted in 1977. However, within the past decade, non-Aroclor, or modern, sources of PCBs have been identified as byproducts of chemical manufacturing of colored pigments, cabinet sealants, and other industrial activities and are found in the environment around the world.

The period when Aroclors were produced (1930–1977) overlaps with that of rapid public-school construction (1950–1980). Of all the public and private schools in the US, 55,000 (46%) were constructed during this period. An estimated 12,960 to 25,920 US schools contain Aroclor PCBs in caulk

alone. ^{9,10} The US EPA does not require schools to test for airborne PCBs. Even if schools choose to test, the EPA has no enforceable threshold concentration of airborne PCBs for which schools must remediate. The EPA does recommend schools should further evaluate PCBs if their levels in air exceed 100–500 ng m⁻³, depending on the age of the students. ¹¹ However, states may require schools to evaluate airborne PCBs at lower levels using different criteria than the EPA's, and parent organizations and teachers' unions may pressure school districts or municipalities to remediate PCBs in their schools. ^{12,13} Additionally, there is evidence that this EPA advisory should not be considered the standard remediation

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threshold. Weitekamp et al. found the rate of exposure to background PCBs through indoor air (i.e., in buildings built after 1979) for children 2–12 years old is two to four times that of adults due to the time children spend in school buildings; this is likely an underestimate for many children given the higher levels of contamination in some schools. Ultimately exposure depends on the amount of time spent inside and an individual's age and body weight, in addition to indoor air concentration. 14

Besides Aroclors, modern PCB sources may exist in overlooked classroom materials such as books, construction paper, and printers due to the pigments that are used in their production. 4,17,18 These Aroclor and non-Aroclor sources contribute to airborne PCBs in schools. 15,19 More than onesixth of the U.S. population (55.4 million) inhabits K-12 buildings during a typical school day, and the quality of school facilities has an impact on human health. 20,21 PCBs are human carcinogens, and exposure is also associated with a variety of neurodevelopmental disorders. 22 Such disorders include hyperactivity, attention disorders, and abnormal scores for conduct as well as deficits in executive function, such as working memory and cognitive flexibility. 23-27 Mice exposed via inhalation to a mixture similar to school air showed modest effects on spatial learning and memory. Furthermore, PCB exposure to the mice stressed the liver and lungs, hematopoietic stem cells, bone marrow cells, and gut microbiota.²⁸ Although diet is commonly assumed to be the largest route of PCB exposure, in the community where this study takes place, inhalation provides a comparable magnitude of exposure due to the levels of PCBs in older schools and the low level of PCBs in their diet. 15,29 For this reason and because young populations are more at risk of adverse health effects, schools have been examined as routes of PCB exposure. 20,21

We hypothesized that PCB concentration and congener profiles differ among rooms within a single building and include both Aroclor and non-Aroclor sources. To our knowledge, such variability has not been published before in peer-reviewed literature but has important implications for the students and adults working in different schoolrooms. Lentifying variability would suggest different sources in different rooms and would also present opportunities for targeted and cost-effective remediation. To test our hypothesis, we measured airborne PCBs in multiple rooms of the same school building. Here, we evaluate concentrations and congener profiles to link them to known source congener profiles. Possible sources include emissions from legacy use of Aroclors in building materials and from modern materials such as paints and sealants.

MATERIALS AND METHODS

Site Description. We collected samples at Columbus Secondary School (CSS), which is in the town of Columbus Junction, Iowa and serves the surrounding rural community. The major employer in the community is a large meat-packing plant that has attracted recent immigrants of Hispanic descent, 36% of the population as of 2018.³⁰ We sampled for airborne PCBs in nine schoolrooms and one location outside (OS) directly above the building's main entrance. The nine schoolrooms include the practice gym (PG), library (L), science room (SR), family consumer science room (FCS), high school gym (HG), math room (MR), art room (AR), art storage room (AS), and social studies room (SS) (Table 1). This community and school system have engaged with our

Table 1. Ten Locations Sampled in This Study and Two Hallway Locations Sampled in a Previous Study, Their Location Codes Used Throughout This Paper, and Their Construction Dates¹⁵

sampling location	location code	construction dates
math room	MR	before 1920
art storage room	AS	before 1920
art room	AR	before 1920
library	L	1920-1970
high school gym	HG	1920-1970
social studies room	SS	1920-1970
family consumer science room	FCS	1920-1970
science room	SR	1920-1970
practice gym	PG	2010s
outside	OS	N/A
high school hallway	HSH	1920-1970
middle school hallway	MSH	before 1920

team since 2006 as part of the Iowa Superfund Research Program. ^{15,19,31–35} This school has hosted passive air samplers at two indoor locations since 2008. Our laboratory previously measured PCBs in these samples and illuminated the importance of inhalation as a major route of exposure for children in this community. ^{15,19} The concentration of PCBs measured in this school was higher than those measured in community homes and in ambient air. PCB congener profiles from air samples collected in two CSS hallways have been published previously and are evaluated more extensively here for Aroclor and non-Aroclor sources. ^{15,36}

Sampler Deployment. We used Harner-style double dome polyurethane foam passive air samplers (PUF–PAS). The Before deployment, we cleaned PUF in sets of three disks per cell with a 1:1 hexane—acetone solution. After drying under N_2 , we wrapped each PUF individually in aluminum foil and stored it at $-4\,^{\circ}$ C. We placed PUF–PAS in each location in triplicate. The results from three samples were not reported because of low surrogate recoveries. We deployed each sampler for 6 weeks (July 1 to August 12, 2019), except for the practice gym samplers which were collected after 3 weeks (July 1 to July 23, 2019) because waxing and renovations were scheduled.

PUF Extraction, Instrument Analysis, and Quality Control. We used accelerated solvent extraction, turbulent evaporation under nitrogen, and acidified silica gel columns to extract and clean the samples, and this is detailed in the Supporting Information (SI). Gas chromatography tandem mass spectrometry (Agilent 7000 Triple Quad with Agilent 7890A GC and Agilent 7693 autosampler) in multiple reaction monitoring mode (MRM) was used for identification and quantification of 209 PCBs as 174 chromatographic peaks. Information about the GC and MS instrument parameters is in the SI. We quantified PCBs using a calibration standard (AccuStandard, New Haven, CT) containing all 209 PCBs (25 ng mL⁻¹ of mono- through trichlorinated congeners, 50 ng mL⁻¹ tetra- through heptachlorinated congeners, and 75 ng \mbox{mL}^{-1} octa- through decachlorinated congeners) and the surrogate (d-PCB 65) and internal (d-PCB 30) standard. We used hexane blanks before and after the calibration run and after sample runs to ensure no carryover. We identified PCBs by comparing samples with the same MRM transition according to retention time (± 0.07 min) except where peak shape or surrogate standard shift dictated otherwise.

We assessed the quality of the data by considering measures of 1) accuracy; 2) representativeness of the intended environment; 3) precision; 4) reproducibility; and 5) comparability to other reports. Accuracy of our methods was previously assessed using standard reference material analysis of certified PCB concentrations in house dust sprinkled on PUF (NIST SRM 2585, Gaithersburg, MD, USA). 15 Reproducibility and precision were assessed by placing triplicates of samplers at each location, side-by-side. Representativeness and precision of our sampling techniques and mass results were assessed with surrogate standards and method blanks. We calculated the limit of quantification (LOQ) as the average congener mass in field blanks (n = 3)plus three times the standard deviation (SD). Method blank PUF (n = 3) was used to monitor the laboratory background levels. Congener masses below LOQ are reported as 0. LOQ values (Table S2) range between 0 and 0.24 ng per congener except for PCB 126 (3.27 ng). The average sum of the method blanks is 1.58 ng. We corrected sample masses for surrogate recoveries that were less than 100%. Average ± standard deviation of surrogate recoveries for PCB 14, d-PCB 65, and PCB 166 was 85.66% \pm 20.03%, 81.54% \pm 19%, and 94.2% \pm 6.76%, respectively. Data generated in this research are available at 10.25820/data.006136.40

Sample Volume. Effective sampling volume is the volume of air passing through the PUF during the time of deployment. Congener-specific effective sampling volumes (V_{eff} , m³) were calculated as a function of the partitioning coefficient (K_{PUF} , unitless), the volume of the PUF (V_{PUF} , m³), the deployment time (t, d), and the sampling rate (R_s , m³ d⁻¹).⁵

$$V_{\text{eff}} = (V_{\text{PUF}} K_{\text{PUF}}) [1 - e^{-(R_s V_{\text{PUF}} K_{\text{PUF}})t}]$$
 (1)

$$R_{\rm s} = (f_{\rm on} \sqrt{\rm WS_{\rm on}} + f_{\rm off} \sqrt{\rm WS_{\rm off}}) \left(\frac{1}{\sqrt[3]{\rm MW}}\right) 10^{[0.0012T + c]}$$
 (2)

The indoor R_s is a function of the molecular weight of the compound (MW, g mol⁻¹), the air temperature $(T, {}^{\circ}C)$, the fraction of the day when ventilation is on or off (f_{on}/f_{off}) , the windspeed when the ventilation is on or off (WS_{on}/WS_{off}) , and the empirical constant of double-dome Harner style samplers (c). According to weather reports from July of 2019, we chose a temperature range of 23–27 °C. ^{5,39} We assumed $f_{\rm on} = 0.36$ and c = 1.326. Mean wind speed, WS_{on} (0.11 m s⁻¹) and WS_{off} (0.07 m s⁻¹), and variance were estimated from previously reported anemometer measurements from the CSS library and measurements conducted in the practice gym. 5,41 The deployment time was t = 21 days for the PG and 42 days for all other rooms. K_{PUF} was averaged for coeluting congeners, and temperature was corrected according to Shoeib 2002 and Herkert 2016 (see the Supporting Information).^{5,41} Airborne PCBs are almost completely in the gas phase. However, the PUF—PAS method captures both gas phase and fine particles. The $V_{\rm eff}$ applies to both phases. ^{39,42}

Air samples were collected from a hallway of the high school wing (n = 13) and a hallway of the middle school wing (n =13) from 2012 to 2015 and analyzed for PCB congeners using the same methods described here, except for the determination of the effective sampling volumes. 15,36 To create a complete and consistent data set, we recalculated the congener-specific effective sampling volumes for each of the 26 earlier measurements using the method here. The recalculation resulted in small decreases in PCB concentrations for that

set of samples, especially for the lower molecular weight congeners. The recalculation also provided us uncertainties in the concentration that are crucial for the positive matrix factorization analysis described later.

Statistical Methods. To assess the uncertainty from parameters used in calculating our concentrations, we implemented a Monte Carlo simulation (Table 2). Windspeed

Table 2. Parameters Used in the Monte Carlo Simulation to Calculate the Concentration of PCBs in Air

parameter	mean value	SD
windspeed (on)	$0.11 \text{ (m s}^{-1})$	0.066
fraction (on)	0.36 (unitless)	0.04
windspeed (off)	$0.07 \text{ (m s}^{-1})$	0.02
fraction (off)	0.64 (unitless)	0.04
temperature	25 (°C)	2
c	1.326 (unitless)	NA
R	8.314 (J K ⁻¹ mol ⁻¹)	NA
$V_{ m PUF}$	$2.295 \times 10^{-4} \text{ (m}^3\text{)}$	NA

standard deviations were determined from measurements of room air flow when ventilation was turned on or off and were similar to what was found in a CFD model for indoor air. Furthermore, subsequent windspeed measurements in the practice gym confirmed the appropriateness of the Monte Carlo simulation range. The means of both the physical measurements and the simulations were 0.11 m s⁻¹ (Figure S1). The windspeed variability is the major contributor to overall uncertainty in the calculated concentrations. The fraction the ventilation was on is the time the school was occupied with a standard deviation of 1 h. We used a standard deviation of 2 °C for the unoccupied summertime school rooms during our deployment period. The standard deviation of the PCB mass was the relative standard deviation (RSD) calculated using the triplicate measurements from the 2019 data. All variables used were found to approximate normal distributions. In the Monte Carlo simulation, a value for each variable was randomly selected from its distribution, and the corresponding concentration was calculated using egs 1 and 2 and egs S1-S3 in the SI. This was repeated 10,000 times to get a distribution of 10,000 values of PCB concentration for each congener in each sample. These distributions were averaged to give a mean concentration, standard deviation, and RSD for each congener in each sample. The total concentration in each room is found by adding the concentrations of each congener in the sample. This is done within the Monte Carlo simulation to give a distribution of total concentrations from which we can find the most probable value and its standard deviation.

We evaluated the differences in the congener profiles using positive matrix factorization (PMF), cosine theta ($\cos \theta$), and principal component analysis (PCA). 43,44 PMF is an analysis tool that decomposes a matrix of data (consisting of samples and PCB congeners) into factor profiles and contributions.⁴⁵ The factor profiles can be combined with each other at different contributions to recreate every sample profile in the data set. PMF has previously been used to identify PCB profiles in sediment, biota, and outdoor air by comparing the factor profiles to known source profiles.^{45–47} Congener and factor profiles are compared using $\cos \theta$. $\cos \theta$ varies from 0 (no correlation) to 1 (complete correlation). PCA creates a smaller number of components that capture most of the variation in the data. 48,49 The data can be described by these components and plotted. Data points that are closer to each other in the plots have more similarities than data points further away.

For all three methods, we normalized the congener concentrations to the sum of the PCB congeners in each sample to evaluate the composition of the profiles. 46 The master data set contained 66 samples and 205 congeners measured in 171 peaks and did not include standards. To allow for a more stable solution to the PMF and an improvement of resolved factors, we removed congeners that had an RSD of greater than 0.50 from the Monte Carlo simulation. An RSD of greater than or equal to 0.50 implies that the concentration could potentially be zero when considering a 95% confidence interval about the mean. Additionally, the matrix was reduced by removing congeners below LOQ in at least 50% of the samples, reducing the number to 133 individual or coeluting congeners. 50-52 PMF requires no zeros in the analyzed data set, so they are replaced with a small number. The remaining zero values in the data matrix were replaced with 10⁻⁶ ng m⁻³ a number smaller than any value in the data matrix.⁴⁴

The uncertainty for each congener in each sample was calculated as the RSD for the congener multiplied by the concentration (Conc_{s,c}). Outdoor samples also had an additional uncertainty due to variations in outdoor windspeed. The final PMF uncertainty (PMF Unc_{s,c}) for each sample, s, and congener, c, was calculated using the following equation

PMF Unc_{s,c} =
$$\sqrt{(\text{Conc}_{s,c} \times \text{RSD}_c)^2 + (\text{LOQ}_{s,c})^2}$$
 (3)

The final data and uncertainty matrices were entered into the EPA's PMF 5.0 software with relaxed criteria. An additional 5% modeling uncertainty was added within the software. Cos θ and PCA were conducted using MATLAB R2019a.

■ RESULTS AND DISCUSSION

Room-to-Room Variation of PCBs. The concentrations of \sum PCB (sum of 171 chromatographic peaks representing the 205 single congeners and coeluting congeners and omitting those used as surrogate and internal standards) in indoor air averaged from 1.54 to 35.75 ng m⁻³ (Figure 1). These

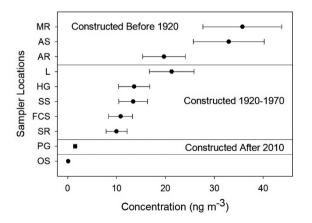


Figure 1. PCB concentration distributions in each location. The dot is the most probable concentration value from the distribution, and the error bars represent one standard deviation from that value. Samplers were placed in the math room (MR), art storage (AS), art room (AR), library (L), social studies (SS), family consumer science (FCS), high school gym (HG), science room (SR), practice gym (PG), and outside (OS).

concentrations are much higher than those found in outdoor air, even in urban industrial areas such as New Bedford Harbor, a Superfund site heavily contaminated with PCBs and one of the largest PCB emission sites in North America. However, the levels we measured in this school are below the U.S. EPA guidance levels and lower than those reported for indoor air in some homes and schools in different communities. The highest individual concentration of airborne PCBs was found in the math room (39.2 ng m⁻³), and the lowest indoor concentration was found in the practice gym (1.24 ng m⁻³). The math room was built before 1920, whereas the practice gym was completed in 2012. We hypothesize the concentration is highest in rooms built before 1920 because renovations were later made with PCB-containing building materials.

Room-to-Room Variation of PCB Congeners. We observed similarities and differences in the congener distributions present in the school rooms (Figure 2 and Figure S2). Some rooms showed similar profiles ($\cos\theta > 0.9$), while some were not similar to any other room. The math room, social studies room, art room, art storage room, family consumer science room, and the high school gym formed one group with similar profiles, and the library and science room formed another. The practice gym and the outside samples did not closely resemble other profiles.

The signals we observe are quite complex and have many peaks in common. No single congener makes up more than 13% of total sample mass except PCB 11 in the practice gym. The practice gym samples are dominated by lower chlorinated congeners PCBs 11, 18 + 30, 44 + 47 + 65, and 52. The practice gym was constructed in 2012, while all other rooms were constructed before 1970. PCB 11 is a non-Aroclor congener found in pigments and materials containing pigments, PCB 18 is an Aroclor congener, and PCB 47 is a non-Aroclor measured in cabinet sealant. PCB 52 is among the top four highest congeners in all the rooms and is known to exist in both Aroclor and non-Aroclor sources. The math room, art room, and art storage room are all dominated by PCBs 61+70+74+76, 90+101+113, and 95. PCBs 70, 74, 95, and 101 were reported in Aroclor 1242, 1248, and 1254. In the library, PCBs 20+28 and 31 are dominant. PCB 28 and 31 are Aroclor congeners. The room-to-room differences in concentrations and congener profiles suggest that different sources are contributing to the airborne PCB emissions from room-toroom. We hypothesized that these differences are significant and due to the variety of historic and modern materials and items present in each room.

To probe the congener profiles and link them to known congener signals of Aroclor mixtures and modern consumer products and building materials, we evaluated the data set (indoor school air collected at MSH and HSH in 2012–2015 and in 2019) using PMF and $\cos \theta$. Three PMF factors reached a stable solution for this data set (Figure 3) and resulted in satisfactory coefficients of determination (R^2) between the modeled and measured concentrations. Only the practice gym was completely described by a single factor. Every other room was described by two or three factors, suggesting that there are a few source types contributing to the PCBs in the different rooms. These three factors were able to reflect the variance found within the rooms.

 $\cos\theta$ analysis and PCA were used to compare the factors to individual Aroclors and mixtures of Aroclors. We used Aroclor data reported by Frame et al. and measured in our

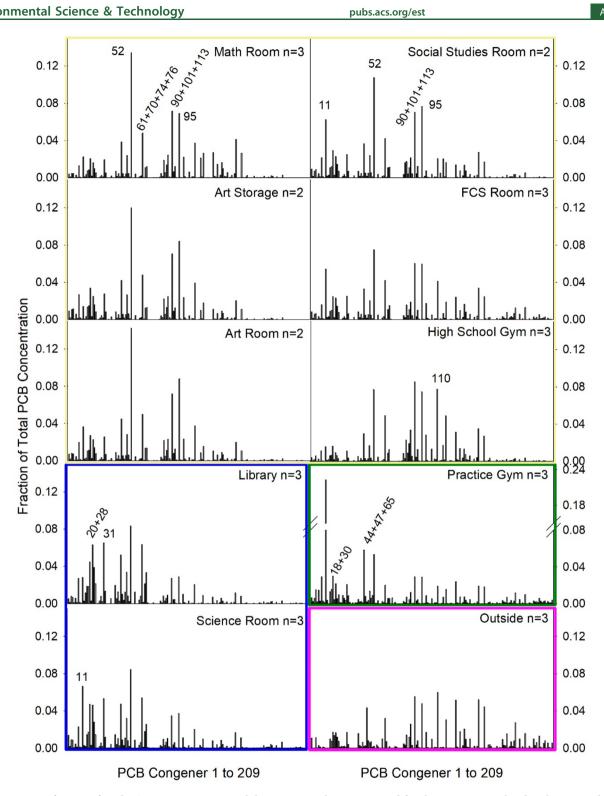


Figure 2. Average fraction of total PCB concentration in each location. Error bars are omitted for clarity. Rooms outlined in the same color share similar profiles ($\cos \theta > 0.9$): the math, social studies, art, art storage, and family consumer science rooms and high school gym in yellow and the science room and library in blue. The practice gym (green) and the outside air (pink) exhibited unique profiles.

laboratory. 33,41 However, PCB profiles of Aroclor emissions differ from the pure mixture due to congener difference in volatility. We hypothesized that PCB emissions were a function of the vapor pressure of each congener, even though we do not expect the PCBs in our school air to be at equilibrium with the sources in each room. To predict what a vaporized Aroclor profile would look like, we multiplied each congener concentration with its subcooled liquid vapor pressure and divided by the sum of the congeners in each sample. 46,59 We tested our hypothesis by comparing the congener emissions profiles from a previously reported laboratory study to the vapor pressure normalized profiles of PCBs in paint colorant.⁴ The $\cos \theta$ values ranged from 0.99 for maroon paint to 0.93 for green paint and exceeded the $\cos \theta$ values between emissions

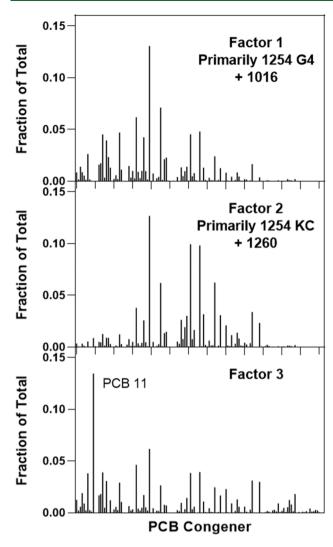


Figure 3. PCB profiles of the three factors that describe CSS indoor school air. Each congener is presented as the fraction of the total amount of all congeners in the factor. Factor 1 is most similar to a mixture of 61% Aroclor 1254 G4 and 39% Aroclor 1254 KC with a residual that resembles Aroclor 1016. Factor 2 is most similar to a mixture of 52% Aroclor 1254 KC and 48% Aroclor 1254 G4 with a residual that resembles Aroclor 1260. Factor 3 includes a stronger signal from PCB 11 and highly chlorinated congeners.

and concentrations without vapor pressure normalization (Table S3). We concluded that normalization of the congener concentrations by the subcooled liquid vapor pressure was the most appropriate data set to evaluate the importance of distinct PCB emission sources in each room.

Two factors were identified as having a signature resembling mixtures of Aroclor 1254. An iterative method was used to calculate combinations of two Aroclors that are most similar to each factor and yielded the highest cos θ . Combinations of vaporized Aroclors 1248 and 1254 fit Factor 1 and Factor 2 well. Aroclor 1254 is more likely to be found in school rooms because it was produced in a much larger amount than Aroclor 1248 and was used in construction applications. 1,60 Factor 1 and Factor 2 most likely represent the mixtures of Aroclors 1254 KC (Lot KC12-638 measured in our lab) and 1254 G4 (reported by Frame et al.) [39% and 61%, respectively, for Factor 1 (cos θ = 0.94) and 52% and 48%, respectively, for Factor 2 (cos θ = 0.93)]. Mixtures of Aroclor 1254 are therefore able to explain most of the data. Factor 3 could not be reproduced with any combination of Aroclors (cos θ < 0.65). Factor 3 is dominated by the non-Aroclor congener PCB 11. It also contains higher contributions from higher chlorinated congeners that are not dominant in the other two factors, many of which are present in paint pigments. We identified Factor 3 as a non-Aroclor signature. All sample, factor, and normalized Aroclor profiles were used in the PCA (Figure S3). In the PCA, samples were not found to be grouped by construction date but instead grouped by similarity to factors and Aroclors. Rooms were found to be grouped in the PCA similarly to the groupings by $\cos \theta$ in Figure 2. All Aroclors besides 1016, 1242, 1248, 1254, and 1260 were separated from the samples and factors. Aroclor 1254 was always found to be grouped with most of the samples.

The differences between the factors and Aroclors are primarily due to sources other than Aroclor 1254.⁶¹ When the 1254 KC and 1254 G4 signal was subtracted from Factor 1, the residual is a signal that resembled Aroclor 1016 ($\cos \theta = 0.82$), consistent with historical use of Aroclor 1016 in fluorescent light fixtures. Factor 2 is also very similar to Aroclor 1254, although when the 1254 KC/1254 G4 signal was removed, the residual resembles Aroclor 1260 ($\cos \theta = 0.85$).

When Aroclor 1254 G4 was subtracted from Factor 3, left behind was the largest amount of residual congeners in terms of percentage of total and number of distinct congeners. Many of the residual congeners are found in Aroclors, but removing

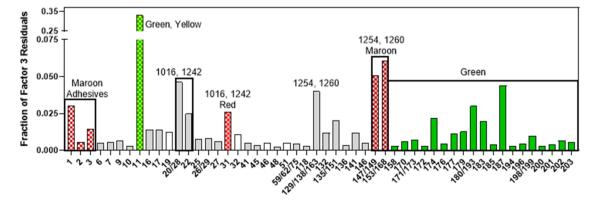


Figure 4. PCBs found in Factor 3 after subtracting Aroclor 1254 G4 from the profile and their potential sources. Congeners associated with maroon, green, yellow, and red paint colorants and with adhesives are indicated by the filled bars. ^{4,64} Congeners found in Aroclors 1016, 1242, 1254, and 1260 at more than 2.5% composition are labeled. Congeners without known sources are indicated by the open bars.

the Aroclor signal shows these congeners may come from non-Aroclor sources. Almost all (92%) of the remaining, residual congeners have been reported in modern paints and/or sealants. 4,56,62-64 The highest congener is the non-Aroclor PCB 11 found primarily in green and yellow colorants and pigments (Figure 4). All the higher chlorinated congeners found in Factor 3 are also found in green colorant, a colorant marked by its high concentrations of higher chlorinated congeners. The family consumer science room is the room with a high contribution of Factor 3. The family consumer science room is painted green. Other congeners are found in Aroclors, but the Aroclor signal does not match Factor 3's profile. Some congeners, PCBs 19, 32, 46, and 51, are not found in colorants, pigments, or sealants. These congeners are in some Aroclors but at small percentages (<2.5% in any Aroclor), and their sources to the classroom air are unknown.

None of the rooms exhibited the exact same factor or source contributions. However, all the rooms have some contribution from each of the sources. We inspected the contribution of Aroclors and the modern sources to each room by summing the amount of each factor that is described by either the Aroclors or the enriched PCBs and the amount that the factor describes a room (Figure 5). Aroclor 1254 is on average the

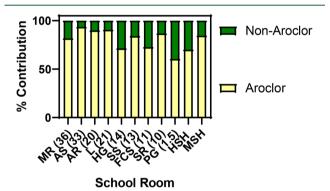


Figure 5. Aroclor 1254 and non-Aroclors are the major contributors to airborne PCB congeners in the CSS school building. Numbers in parentheses are the total concentrations measured in each room in ng $\,\mathrm{m}^{-3}$.

largest source of PCBs. These findings correspond with the results from the previous sampling of CSS; Aroclor 1254 was identified in the hallway samples collected between 2012 and 2015. Additionally, while many rooms (~70%) group together in a PCA, other rooms like the practice gym, library, and science room have distinctively different and diverse congener signals (Figure S4). Our analysis indicates that different rooms can have different primary sources of PCBs that may be considered when approaching remediation. In this school, modern sources make a significant contribution to the total PCBs found in air. These modern sources continue to be produced and used in schools, yet they may be the easiest to remediate or remove.

High PCB concentration in school air is very expensive to remediate and has led to school demolitions and closures across the United States. ¹³ In New York City, over \$800,000,000 was spent to remove PCB-contaminated light ballasts. ⁶⁵ Understanding how PCBs in indoor school air vary from room-to-room can help improve methods of identifying sources and inform decisions to remediate, close, or demolish a school. Here we developed a rigorous approach to evaluate

room-specific school air for prioritizing PCB source testing and remediation. Our method uses noninvasive sampling, quantification of all 209 congeners, and statistical analysis to understand room-to-room variation in PCB concentration and congener profiles. We found that school construction year alone does not explain PCB concentrations in air due to variation from room to room. Although the school we examined had PCB levels below EPA-suggested action levels, our analysis indicates both Aroclor and non-Aroclor materials are currently releasing PCBs within the school. Schools with low levels of PCBs still have reason to consider remediation due to the toxicity of PCBs and the amount of time children spend in school. Our method represents a first step toward prioritizing rooms to remediate, effectively and efficiently reducing PCB sources in schools.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c08149.

Additional details of analytical and statistical methods, as well as full data set of limit of quantification for each congener (PDF)

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Notes

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■ REFERENCES

- (1) Erickson, M. D.; Kaley, R. G. Applications of polychlorinated biphenyls. *Environ. Sci. Pollut. Res.* **2011**, *18* (2), 135–151.
- (2) Brown, K. W.; Minegishi, T.; Cummiskey, C. C.; Fragala, M. A.; Hartman, R.; MacIntosh, D. L. PCB remediation in schools: a review. *Environ. Sci. Pollut. Res.* **2016**, 23 (3), 1986–1997.
- (3) Code U. S., Chapter 53 Toxic Substance Control Act, SubChapter 1 Control of Toxic Substances. In *Title 15*, 2009 ed.; Congress, U. S., Ed.; U.S. Government Publishing Office: 1976.
- (4) Jahnke, J. C.; Hornbuckle, K. C. PCB Emissions from Paint Colorants. *Environ. Sci. Technol.* **2019**, 53 (9), 5187–5194.
- (5) Herkert, N. J.; Hornbuckle, K. C. Effects of room airflow on accurate determination of PUF-PAS sampling rates in the indoor environment. *Environ. Sci. Process Impacts* **2018**, 20 (5), 757–766.
- (6) Cui, S.; Qi, H.; Liu, L. Y.; Song, W. W.; Ma, W. L.; Jia, H. L.; Ding, Y. S.; Li, Y. F. Emission of unintentionally produced polychlorinated biphenyls (UP-PCBs) in China: Has this become the major source of PCBs in Chinese air? *Atmos. Environ.* **2013**, *67*, 73–79.
- (7) Guo, J.; Capozzi, S. L.; Kraeutler, T. M.; Rodenburg, L. A. Global Distribution and Local Impacts of Inadvertently Generated Polychlorinated Biphenyls in Pigments. *Environ. Sci. Technol.* **2014**, 48 (15), 8573–8580.
- (8) Zhao, S. Z.; Jones, K. C.; Li, J.; Sweetman, A. J.; Liu, X.; Xu, Y.; Wang, Y.; Lin, T.; Mao, S. D.; Li, K. C.; Tang, J.; Zhang, G. Evidence for Major Contributions of Unintentionally Produced PCBs in the Air of China: Implications for the National Source Inventory. *Environ. Sci. Technol.* **2020**, *54* (4), 2163–2171.
- (9) Herrick, R. F.; Stewart, J. H.; Allen, J. G. Review of PCBs in US schools: a brief history, an estimate of the number of impacted schools, and an approach for evaluating indoor air samples. *Environ. Sci. Pollut. Res.* **2016**, 23 (3), 1975–1985.
- (10) MacIntosh, D. L.; Minegishi, T.; Fragala, M. A.; Allen, J. G.; Coghlan, K. M.; Stewart, J. H.; McCarthy, J. F. Mitigation of building-related polychlorinated biphenyls in indoor air of a school. *Environ. Health* **2012**, *11*, 24.
- (11) United States Environmental Protection Agency Exposure Levels for Evaluating Polychlorinated Biphenyls (PCBs) in Indoor School Air. https://www.epa.gov/pcbs/exposure-levels-evaluating-polychlorinated-biphenyls-pcbs-indoor-school-air (accessed 2020-03-14).
- (12) Health, V. D. o. *Indoor Air Sampling for PCBs in Vermont Schools*; Vermont Agency of Education: 2014; p 1. healthvermont.gov (accessed 2021-05-17).
- (13) Osterberg, D.; Scammell, M. K. PCBs in schools-where communities and science come together. *Environ. Sci. Pollut. Res.* **2016**, 23 (3), 1998–2002.
- (14) Weitekamp, C. A. P.; Linda, J.; Carlson, L. M.; DeLuca, N. M.; Cohen Hubal, E. A.; Lehmann, G. M. A state-of-the-science review of polychlorinated biphenyl exposures at background levels: Relative

- contributions of exposure routes. Sci. Total Environ. 2021, 776, 145912.
- (15) Marek, R. F.; Thorne, P. S.; Herkert, N. J.; Awad, A. M.; Hornbuckle, K. C. Airborne PCBs and OH-PCBs inside and outside urban and rural U.S. schools. *Environ. Sci. Technol.* **2017**, *51* (14), 7853–7860.
- (16) Thomas, K. X. J.; Williams, R.; Jones, P.; Whitaker, D. *Polychlorinated biphenyls (PCBs) in school buildings: Sources, environmental levels, and exposure*; EPA/600/R-12/051; U.S. Environmental Protection Agency: 2012.
- (17) Vorkamp, K. An overlooked environmental issue? A review of the inadvertent formation of PCB-11 and other PCB congeners and their occurrence in consumer products and in the environment. *Sci. Total Environ.* **2016**, *541*, 1463–1476.
- (18) Rodenburg, L.; Guo, J.; Christie, R. Polychlorinated biphenyls in pigments: inadvertent production and environmental significance. *Color. Technol.* **2015**, *131* (5), 353–369.
- (19) Ampleman, M. D.; Martinez, A.; DeWall, J.; Rawn, D. F. K.; Hornbuckle, K. C.; Thorne, P. S. Inhalation and Dietary Exposure to PCBs in Urban and Rural Cohorts via Congener-Specific Measurements. *Environ. Sci. Technol.* **2015**, 49 (2), 1156–1164.
- (20) Eubig, P. A.; Aguiar, A.; Schantz, S. L. Lead and PCBs as risk factors for attention deficit/hyperactivity disorder. *Environ. Health Perspect.* **2010**, *118* (12), 1654–67.
- (21) Brauner, E. V.; Andersen, Z. J.; Frederiksen, M.; Specht, I. O.; Hougaard, K. S.; Ebbehoj, N.; Bailey, J.; Giwercman, A.; Steenland, K.; Longnecker, M. P.; Bonde, J. P. Health Effects of PCBs in Residences and Schools (HESPERUS): PCB health Cohort Profile. *Sci. Rep.* 2016, 6, 24571.
- (22) International Agency for Research on Cancer *Polychlorinated Biphenyls and Polybrominated Biphenyls Vol.* 107; World Health Organization: 2015.
- (23) Schantz, S. L.; Gasior, D. M.; Polverejan, E.; McCaffrey, R. J.; Sweeney, A. M.; Humphrey, H. E.; Gardiner, J. C. Impairments of memory and learning in older adults exposed to polychlorinated biphenyls via consumption of Great Lakes fish. *Environ. Health Perspect.* **2001**, *109* (6), 605–11.
- (24) Wang, B. L.; Pang, S. T.; Sun, J. P.; Zhang, X. L.; Li, X. L.; Sun, Y. G.; Lu, X. M.; Zhang, Q. Levels of polychlorinated biphenyls in settled house dust from urban dwellings in China and their neurodevelopmental effects on preschool-aged children. *Sci. Total Environ.* 2015, 505, 402–408.
- (25) Sethi, S.; Keil, K. P.; Chen, H.; Hayakawa, K.; Li, X. S.; Lin, Y. P.; Lehmler, H. J.; Puschner, B.; Lein, P. J. Detection of 3,3 '-Dichlorobiphenyl in Human Maternal Plasma and Its Effects on Axonal and Dendritic Growth in Primary Rat Neurons. *Toxicol. Sci.* 2017, 158 (2), 401–411.
- (26) Klocke, C.; Lein, P. J. Evidence Implicating Non-Dioxin-Like Congeners as the Key Mediators of Polychlorinated Biphenyl (PCB) Developmental Neurotoxicity. *Int. J. Mol. Sci.* **2020**, *21* (3), 1013.
- (27) Pessah, I. N.; Lein, P. J.; Seegal, R. F.; Sagiv, S. K. Neurotoxicity of polychlorinated biphenyls and related organohalogens. *Acta Neuropathol.* **2019**, *138* (3), 363–387.
- (28) Wang, H.; Adamcakova-Dodd, A.; Flor, S.; Gosse, L.; Klenov, V. E.; Stolwijk, J. M.; Lehmler, H. J.; Hornbuckle, K. C.; Ludewig, G.; Robertson, L. W.; Thorne, P. S. Comprehensive Subchronic Inhalation Toxicity Assessment of an Indoor School Air Mixture of PCBs. *Environ. Sci. Technol.* **2020**, *54* (24), 15976–15985.
- (29) Saktrakulkla, P.; Lan, T.; Hua, J.; Marek, R. F.; Thorne, P. S.; Hornbuckle, K. C. Polychlorinated Biphenyls in Food. *Environ. Sci. Technol.* **2020**, *54* (18), 11443–11452.
- (30) Bureau, U. S. C. In *Demographic Analysis*; December 15, 2020 ed.; 2020.
- (31) Marek, R. F.; Thorne, P. S.; Wang, K.; Dewall, J.; Hornbuckle, K. C. PCBs and OH-PCBs in serum from children and mothers in urban and rural U.S. communities. *Environ. Sci. Technol.* **2013**, *47* (7), 3353–61.
- (32) Marek, R. F.; Thorne, P. S.; DeWall, J.; Hornbuckle, K. C. Variability in PCB and OH-PCB serum levels in children and their

- mothers in urban and rural U.S. communities. *Environ. Sci. Technol.* **2014**, 48 (22), 13459–67.
- (33) Koh, W. X.; Hornbuckle, K. C.; Thorne, P. S. Human serum from urban and rural adolescents and their mothers shows exposure to polychlorinated biphenyls not found in commercial mixtures. *Environ. Sci. Technol.* **2015**, 49 (13), 8105–8112.
- (34) Koh, W. X.; Hornbuckle, K. C.; Wang, K.; Thorne, P. S. Serum polychlorinated biphenyls and their hydroxylated metabolites are associated with demographic and behavioral factors in children and mothers. *Environ. Int.* **2016**, *94*, 538–545.
- (35) Koh, W. X.; Hornbuckle, K. C.; Marek, R. F.; Wang, K.; Thorne, P. S. Hydroxylated polychlorinated biphenyls in human sera from adolescents and their mothers living in two U.S. Midwestern communities. *Chemosphere* **2016**, *147*, 389–95.
- (36) Marek, R. F.; Thorne, P. S.; Herkert, N. J.; Awad, A. M.; Hornbuckle, K. C. In *Dataset for airborne PCBs and OH-PCBs inside and outside urban and rural U.S. schools*; University of Iowa: 2020.
- (37) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, 38 (1), 34–41.
- (38) Pozo, K.; Harner, T.; Wania, F.; Muir, D. C. G.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: Results from the GAPS study. *Environ. Sci. Technol.* **2006**, 40 (16), 4867–4873.
- (39) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36* (19), 4142–4151.
- (40) Bannavti, M. K. J.; Jacob, C.; Marek, R. F.; Hornbuckle, K. C. In Dataset for Room-to-Room Variability of Airborne PCBs in Schools and the Application of Air Sampling for Targeted Source Evaluation; University of Iowa: 2021.
- (41) He, S.; Kenchi, S.; Jeanblanc, E.; Murillo, E. Report of Field trip to Columbus Junction. Iowa NSF EPSCoR Energy Utilization Platform Building Science Plank and Center for Building Energy Research. In *Iowa NSF EPSCoR 2015 Annual Report Year 4* (2015). *Iowa NSF EPSCoR Reports*; 6th ed.; Iowa EPSCoR, Heindel, T. J., Eds.; University of Iowa: 2014.
- (42) Herkert, N. J.; Martinez, A.; Hornbuckle, K. C. A Model Using Local Weather Data to Determine the Effective Sampling Volume for PCB Congeners Collected on Passive Air Samplers. *Environ. Sci. Technol.* **2016**, *50* (13), 6690–6697.
- (43) Norris, G.; Duvall, R.; Brown, S.; Song, B. Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide; 2014.
- (44) Saba, T.; Su, S. Tracking polychlorinated biphenyls (PCBs) congener patterns in Newark Bay surface sediment using principal component analysis (PCA) and positive matrix factorization (PMF). *J. Hazard. Mater.* **2013**, *260*, *634*–43.
- (45) Paatero, P.; Tapper, U. Positive Matrix Factorization a Nonnegative Factor Model with Optimal Utilization of Error-Estimates of Data Values. *Environmetrics* 1994, 5 (2), 111–126.
- (46) Rodenburg, L. A.; Meng, Q. Source apportionment of polychlorinated biphenyls in Chicago air from 1996 to 2007. *Environ. Sci. Technol.* **2013**, 47 (8), 3774–80.
- (47) Du, S.; Belton, T.; Rodenburg, L. Source Apportionment of Polychlorinated Biphenyls in the Tidal Delaware River. *Environ. Sci. Technol.* **2008**, *42*, 4044–51.
- (48) Jin, R. H.; Park, S. U.; Park, J. E.; Kim, J. G. Polychlorinated Biphenyl Congeners in River Sediments: Distribution and Source Identification Using Multivariate Factor Analysis. *Arch. Environ. Contam. Toxicol.* **2012**, *62* (3), 411–423.
- (49) Thurston, G. D.; Spengler, J. D. A Quantitative Assessment of Source Contributions to Inhalable Particulate Matter Pollution in Metropolitan Boston. *Atmos. Environ.* **1985**, *19* (1), 9–25.
- (50) Rodenburg, L. A.; Winstanley, I.; Wallin, J. M. Source Apportionment of Polychlorinated Biphenyls in Atmospheric Deposition in the Seattle, WA, USA Area Measured with Method 1668. Arch. Environ. Contam. Toxicol. 2019, 77 (2), 188–196.

- (51) Chitsaz, M.; Fennell, D. E.; Rodenburg, L. A. Sources of polychlorinated biphenyls to Upper Hudson River sediment post-dredging. *Chemosphere* **2020**, 259, 127438.
- (52) Du, S. Y.; Rodenburg, L. A. Source identification of atmospheric PCBs in Philadelphia/Camden using positive matrix factorization followed by the potential source contribution function. *Atmos. Environ.* **2007**, *41* (38), 8596–8608.
- (53) Martinez, A.; Hadnott, B. N.; Awad, A. M.; Herkert, N. J.; Tomsho, K.; Basra, K.; Scammell, M. K.; Heiger-Bernays, W.; Hornbuckle, K. C. Release of Airborne Polychlorinated Biphenyls from New Bedford Harbor Results in Elevated Concentrations in the Surrounding Air. *Environ. Sci. Technol. Lett.* **2017**, *4* (4), 127–131.
- (54) Zhang, X.; Diamond, M. L.; Robson, M.; Harrad, S. Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. *Environ. Sci. Technol.* **2011**, 45 (8), 3268–74.
- (55) Audy, O.; Melymuk, L.; Venier, M.; Vojta, S.; Becanova, J.; Romanak, K.; Vykoukalova, M.; Prokes, R.; Kukucka, P.; Diamond, M. L.; Klanova, J. PCBs and organochlorine pesticides in indoor environments A comparison of indoor contamination in Canada and Czech Republic. *Chemosphere* **2018**, *206*, 622–631.
- (56) Hu, D.; Hornbuckle, K. C. Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol.* **2010**, 44 (8), 2822–2827.
- (57) Frame, G. M.; Cochran, J. W.; Bøwadt, S. S. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J. High Resolut. Chromatogr. 1996, 19 (12), 657–668.
- (58) Herkert, N. J.; Jahnke, J. C.; Hornbuckle, K. C. Emissions of tetrachlorobiphenyls (PCBs 47, 51, and 68) from polymer resin on kitchen cabinets as a non-Aroclor source to residential air. *Environ. Sci. Technol.* **2018**, 52 (9), 5154–5160.
- (59) Fischer, R. C.; Wittlinger, R.; Ballschmiter, K. Retention-Index Based Vapor-Pressure Estimation for Polychlorobiphenyl (Pcb) by Gas-Chromatography. *Fresenius' J. Anal. Chem.* **1992**, 342 (4–5), 421–425.
- (60) Durfee, R.; Contos, G.; Whitmore, F.; Barden, J.; Hackman, E.; Westin, R. PCBs in the United States—industrial use and environmental distributions. US Environmental Protection Agency; EPA 560/6-76-005; NTIS No. PB-252 012; Washington, DC, 1976.
- (61) Rodenburg, L. A.; Delistraty, D.; Meng, Q. Polychlorinated biphenyl congener patterns in fish near the Hanford Site (Washington State, USA). *Environ. Sci. Technol.* **2015**, 49 (5), 2767–75.
- (62) Anezaki, K.; Kannan, N.; Nakano, T. Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments. *Environ. Sci. Pollut. Res.* **2015**, 22 (19), 14478–88.
- (63) Anezaki, K.; Nakano, T. Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments. *Environ. Sci. Pollut. Res.* **2014**, *21*, 998–1009.
- (64) Anezaki, K.; Nakano, T. Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples. *J. Hazard. Mater.* **2015**, 287, 111–117.
- (65) THE COUNCIL OF THE CITY OF NEW YORK, Report of the Finance Division on the Fiscal 2019 Preliminary Capital Budget, the February 2018 Proposed Amendment to the FY2015—2019 Five-Year Capital Plan, and the Fiscal 2018 Preliminary Mayor's Management Report for the Department of Education and the School Construction Authority. https://council.nyc.gov/budget/wpcontent/uploads/sites/54/2018/03/FY19-Department-of-Education-and-the-School-Construction-Authority.pdf (2020-12-01).