

Article

Children's Exposure to Volatile Organic Compounds: A Comparative Analysis of Assessments in Households, Schools, and Indoor Swimming Pools

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Abstract: Chemical pollution is an increasing worldwide concern, with children being especially vulnerable to the harmful effects of air pollution. This study aimed to characterize the mixture of volatile organic compounds (VOCs) present in indoor air across residential, educational, and recreational settings. It analyzed data on VOC concentrations from previous sampling campaigns conducted in households with children, primary schools, and indoor swimming pools (70 buildings, 151 indoor spaces) in northern Portugal. The findings reveal the co-occurrence of 16 VOCs (1,2,4-trimethylbenzene, benzene, ethylbenzene, m/o/p-xylenes, styrene, toluene, tetrachloroethylene, 2-ethylhexanol, butanol, acetophenone, ethyl acetate, benzaldehyde, decanal, nonanal, 1-methoxy-2-propanol and limonene) across all three settings, primarily associated to emissions from building materials and detergents. However, distinct patterns were also observed in the VOCs detected across the three indoor environments: in homes, the predominant VOCs were primarily released from cleaning and fragranced products; in schools, from ammonia-based cleaners and occupant activities; and in swimming pools, the predominant airborne chemicals were disinfection by-products resulting from the chemical dynamics associated with water disinfection. Overall, the findings highlight the need for additional research to deepen our understanding of the risks posed by combined exposure to multiple indoor air chemicals for children. These results also underscore the importance of developing and enforcing regulations to monitor VOC levels in environments frequented by children and implementing preventive measures to minimize their exposure to harmful chemicals.

Keywords: chemical air pollution; children; combined exposure; indoor environment; volatile organic compounds



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1. Introduction

Pollution has been presented as the leading environmental factor contributing to illness and early mortality in the world today [1]. According to the World Health Organization (WHO), around two-thirds of the 12.6 million annual deaths attributed to the environment are due to noncommunicable diseases (NCDs), and 23% of global deaths could be avoided by promoting healthier environments [2]. In particular, chemical pollution has been singled out as a great and growing global problem, with its impact on the overall disease burden likely being underestimated [1,3]. The need for effective actions to mitigate chemical pollution in order to reduce the number of deaths and illnesses caused by hazardous chemicals by 2030 is one of the environmental and health priorities considered in the United Nations 2030 Agenda for Sustainable Development [4].

The level of air pollution in indoor environments is reported to often exceed outdoor levels, mainly due to the presence of important indoor emissions sources and/or to the

existence of conditions that promote the accumulation of pollutants indoors (e.g., buildings with insufficient ventilation rates) [5–8]. The most commonly reported indoor sources of hazardous chemicals are building materials, furniture, tobacco smoking, cleaning products, other fragranced consumer products (e.g., air fresheners), and occupant activities [9,10]. In turn, motorized transport, industry, construction, agriculture, and waste management are among the main outdoor air pollution sources. In fact, due to the myriad of sources of emissions and diversity of building characteristics, among other factors that govern indoor pollutant levels, people are likely to be exposed to a complex mixture of different harmful individual indoor air pollutants exhibiting complex temporal and spatial fluctuations [10–12].

The WHO has established indoor air quality (IAQ) guidelines for some individual chemical air contaminants. These have been listed as selected pollutants, including a few volatile organic compound (VOC) species (naphthalene, trichloroethylene, and tetrachloroethylene), formaldehyde, carbon monoxide (CO), nitrogen dioxide (NO₂), polycyclic aromatic hydrocarbons (PAHs), and radon [13]. However, the existing evidence demonstrates that the list of concerning chemicals in indoor air is much broader. In fact, for some pollutants, the available information is insufficient to derive IAQ guidelines levels, but the toxicological evidence supports that these should be subject of studies aiming to carry out realistic assessments of co-exposures and related health risks [14]. In this regard, recently, a WHO Europe initiative identified a list of 17 priority chemicals that need to be considered in further assessments of exposure to multiple chemicals through the air in indoor settings for children [14,15]. Most of the listed substances are VOCs, a main category of airborne hazardous substances that have been linked to both acute and chronic adverse health impacts, including sensory and skin irritation, headaches, respiratory symptoms, asthma development and exacerbation, and cancer [16–18]. In fact, various VOCs, including alkanes, aromatics, and terpenoids, are commonly found indoors, originating from sources like building materials, cleaning, cooking, occupant activities, consumer products, and outdoor transport. The types and concentrations of VOCs are very likely to vary by environment and are very likely to fluctuate spatially and seasonally due to factors like temperature, humidity, air exchange rate, building structure, and human activities conducted indoors [19].

People typically spend about 90% of their time in indoor spaces, and depending on individual context and lifestyle, different proportions of their time are spent in a variety of microenvironments such as home, work, school, and other public and private buildings [20]. The patterns of exposure that take place in different microenvironments and the combined exposure with the mixture of hazardous chemicals that co-exist in the indoor air in each microenvironment can be determinants of IAQ-related health outcomes [21–25]. Thus, efforts targeting a thorough understanding of chemical air pollution patterns in real-world environments are essential for establishing representative risk assessment protocols and effective policies to reduce emissions and protect health. In spite of the need for a comprehensive approach, estimates of population exposure based on measured indoor air pollution data have often been restricted to a limited number of substances and/or to a single type of indoor environment.

Children are particularly vulnerable to hazardous chemicals compared to adults due to a combination of physiological (immature respiratory and immune systems and higher daily inhalation rate), behavioral (hand-to-mouth behavior), and social characteristics [26–28]. This study aimed to evaluate both the qualitative and quantitative patterns of VOCs found in three different indoor settings for children of the same geographical area in order to characterize and compare the mixture of VOCs to which children may be exposed in each microenvironment. In particular, this work gathers the data obtained from recent assessment plans conducted in homes of families with infants, in primary schools, and in indoor swimming pools located in Northern Portugal.

2. Materials and Methods

2.1. Study Design and Characteristics of the Sampled Buildings

Environmental data were sourced from INEGI's database, which has been developed over the last decade based on the outcomes from indoor air quality assessments conducted in several buildings across the Northern Portugal. Based on the aim of this study and availability of the raw data for VOCs, this work focused on three different types of microenvironments of great interest for child exposure: households of families with children, primary schools, and public indoor swimming pools (representing an indoor recreational setting). Thus, the data from the HEALS—Health and Environment-wide Associations based on Large population Surveys (EC project), ARIA—How Indoor Air Quality Affect Children Allergies and Asthma (National project, [29]), and HEBE—Health, Comfort and Energy in the Built Environment (National project, [30]) projects were used. All these projects included comprehensive IAQ assessment plans conducted for a sample of buildings (homes/residential buildings: $n = 30$, primary schools: $n = 20$, indoor swimming pools: $n = 20$) located in the same geographical area (Northern Portugal). These 3 studies were designed to reduce the possibility of the introduction of bias to the representativeness of the buildings during the recruitment/selection processes. For residential buildings, the recruitment of participant families was conducted in 4 local public maternity hospitals. The selection of homes was conducted based on the project's eligibility criteria, which included an agreement to provide biological samples. The first 30 families in the cohort who expressed an interest in receiving home-visit IAQ assessments were included in the study. Then, the main aim of the ARIA was to study the relationship between indoor environmental conditions in schools and health effects on children, with a special focus on asthma. The target number of classrooms was determined to ensure representativeness based on the estimated sample size of children ($n = 1600$), assuming an asthma prevalence value in children of 10%. Out of 53 public primary schools existing in the Porto Municipality at the time of the study, 20 were selected for evaluation. Finally, 20 swimming pools managed by 17 municipalities and 1 sport institution were included in the study. The location of buildings studied is presented in Figure S1 in the Supplementary Materials.

Assessment plans conducted in the 3 studies included a walkthrough inspection, building survey, and sampling activities. For each type of surveyed building, a specific checklist was developed for data collection during the comprehensive building survey. The checklists included a large set of questions related to specific topics, such as characteristics of the outdoor environment surrounding the building, building age and construction, heating and ventilation systems and condition, past and present visible problems (e.g., moisture on the walls), and the existence of evident indoor pollution sources. Specific information about the indoor spaces studied and their use was the object of special attention. For homes, 2 rooms in each dwelling were surveyed (60 sampling points): infant bedroom and a second room (for most cases, the living room) as described in a previous publication [31]. In the assessments conducted in schools, a total of 71 classrooms (2–4 rooms per school building) for the third and/or fourth grades (children aged 8–10 years) were investigated [29]. For indoor swimming pools, the main room housing the biggest swimming pool in the facility was the target of the study [30]. All pools surveyed employed a chlorine-based product as the primary disinfectant, but 8 used chlorination in combination with UV treatment. Data on the main characteristics of the buildings and indoor spaces considered in this study are summarized in Table 1.

Table 1. Summary of the characteristics of the buildings and indoor spaces investigated in this study.

Characteristics	Households (n = 30)		Schools (n = 20)		Swimming Pools (n = 20)	
	n (%)	Mean (SD)	n (%)	Mean (SD)	n (%)	Mean (SD)
Building						
Period of construction						
Before 1950	1 (3)		3 (15)		0 (0)	
1950–1980	4 (13)		14 (70)		2 (20)	
1980–2010	19 (63)		3 (15)		18 (80)	
After 2010	6 (20)		0 (0)		0 (0)	
Ventilation						
Natural	30 (100)		19 (95)		14 (70)	
Mechanical	0 (0)		1 (5)		20 (100)	
Air fresheners	15 (50)		1 (5)		3 (15)	
Indoor plants	19 (63)		1 (5)		4 (20)	
Surrounding outdoor pollution sources						
Traffic-related	29 (97)		16 (80)		20 (100)	
Busy road	6 (20)		15 (75)		6 (30)	
Highway	1 (3)		1 (5)		2 (10)	
Car parking	26 (87)		4 (20)		20 (100)	
Gas stations	1 (3)		3 (15)		2 (10)	
Others	16 (53)		1 (5)		6 (30)	
Cleaning						
Bleach or detergent with bleach	23 (77)		4 (20)		11 (55)	
Spray	2 (7)		0 (0)		0 (0)	
Liquid	22 (73)		4 (20)		11 (55)	
Detergent with ammonia	7 (23)		9 (45)		1 (5)	
Spray	0 (0)		8 (40)		0 (0)	
Liquid	7 (23)		1 (5)		1 (5)	
Other detergent/cleaning products	29 (97)		20 (100)		16 (80)	
Spray	3 (10)		0 (0)		0 (0)	
Liquid	27 (90)		20 (100)		16 (80)	
Wax/furniture polish	6 (20)		3 (15)		2 (10)	
Spray	0 (0)		n.i.		0 (0)	
Liquid	6 (20)		n.i.		2 (10)	
Indoor spaces [‡]						
Floor area (m ²)		19 (9)		51 (8)		1161 (556)
Ceiling height (m)		3 (0)		3 (0)		7 (2)
Volume (m ³)		50 (23)		172 (29)		8856 (6453)
Interior of the room remodeled, renovated, or painted in the past 12 months	14 (23)		14 (20)		7 (35)	
Signs of pathologies						
Physical	3 (5)		31 (44)		13 (65)	
Moisture-related	1 (2)		13 (18) *		18 (90)	
Number of occupants		3 (1)		21 (3)		16 (10)

n (%) refers to the total number of buildings/rooms and respective percentages for the valid cases. For characteristics that are metric variables, the mean, minimum, and maximum values registered are presented. n.i. indicates that no information is available; SD, standard deviation. [‡] Households: bedrooms and second rooms (n = 60); schools: classrooms (n = 71); swimming pools: main room (n = 20). * Visible mold growth, noticeable mold odor, or visible damp spots.

The assessment of IAQ in homes was conducted from July 2018 to June 2019. In schools, sampling works were carried out in the periods between January and April 2014 and between October 2014 and January 2015. And indoor swimming pools were surveyed in 2 sampling campaigns during the cold (January–March) and warm (May–July) seasons of 2018. For all buildings surveyed, IAQ assessments were conducted under the representative conditions of occupancy, use, cleaning, and ventilation.

2.2. VOC Sampling and Laboratorial Analysis

The methodology for VOC sampling was selected in accordance with the typical duration of occupation of the indoor environments under study. Since homes and schools are the two indoor environments in which children typically spend the greater part of their daily time, passive sampling was preferred. A period of 5 to 7 days was considered in households [31]. To reproduce the typical school week, from Monday morning to Friday afternoon, in schools, samples were collected over a 5-day period [29]. For both environments, the assessment consisted of installing duplicate stainless-steel tubes containing Tenax TA (60/80 mesh) with glass wool at one end and a sorbent retaining gauze in the open in all sampling locations, chosen in accordance with the standard ISO 16000-1:2004 [32]. Samples were collected from locations at least 1 m away from a wall, a door, or an active heating system, and were as representative as possible of the children's breathing zones, specifically:

- Homes: for bedrooms, near the beds of children, with samplers being placed at a height similar to the location of the pillow (0.5–1.0 m); and for a second room (typically the living room) in the area where children spend most of their time when they are not at the bedroom, at a height of 0.5–0.9 m;
- Schools: in the classrooms at a height of about 1.0–1.5 m above the floor.

After sampling, the tubes were thermally desorbed (model STD 33.50, DANI Instruments, Italy). Subsequently, the VOC content in the samples was quantified following the ISO 16017-2:2003 [33], using a capillary column (HP-5: 50 m × 0.2 mm × 0.5 µm) by gas chromatography (model 6890N, Agilent Technologies, USA) coupled to a mass spectrometer detector (model 5975C, Agilent Technologies, Santa Clara, CA 95051, USA).

For swimming pools, the active approach of 1 h sampling was employed since the typical exposure of attendants occurs for shorter periods, as described elsewhere [30]. Air sampling of a 1 h duration was systematically conducted in two locations: (i) in the boundary layer 10 cm above the water surface and (ii) the surrounding environment approximately 1.0 m to the pool and 1.5 m above the ground. The locations were chosen with the aim of obtaining approximate exposure concentrations in the typical breathing zones of users both during swimming activities and their time spent in the space surrounding the pool. VOCs were collected in 2 periods on a weekday: (1) in the morning, during the first hour of swimming activity in the day and (2) in the evening, in the period of expected high attendance of the swimming pool. In this case, air sampling was carried out using stainless-steel sampling tubes containing Tenax TA (60/80 mesh) coupled to a pump (AirChek XR5000, SKC, Inc., Pittsburgh, PA 15330, USA) defining a flow rate set-up at 60–70 mL/min. The samples were analyzed following the standard ISO 16000-6: 2011 [34], i.e., tubes were thermally desorbed (DANI, model MASTER) on-line with gas chromatography (Agilent Technologies, USA, model 7890A) coupled to a mass spectrometer detector (Agilent Technologies, USA, model 5975C) for VOC identification and quantification (GC/MSD). The capillary column used was an HP5MS (50 m × 0.2 mm × 0.33 µm). Cyclodecane was injected in all tubes as the internal standard and diffusion coefficients and flow rates were adjusted for the mean temperature registered during samplings. The total VOC (TVOC) of the samples was defined as the sum of the concentration of all detected compounds presenting a retention time comprising n-hexane and n-hexadecane, using the specific response factor for the identified compounds. The toluene response factor was used for the remaining cases. For the determination of VOCs, the laboratory performed quality control tests on a daily basis through the use of control charts. The analytical method demonstrates linearity in the range of 10–5000 ng for toluene, with a confidence level of 95%. The recovery was determined to be higher than 99% for VOCs. Field blanks were taken, and tubes were analyzed for quality assurance purposes. The limit of detection (LOD) was calculated as one-third of the value of the limit of quantification (LOQ). The LOQ was defined as 10 times the standard deviation of the results from a series of at least 12 replicate tubes spiked with the compounds of interest at levels at or near the quantification limit. The LOD values (µg/m³) were independently determined for a limited list

of compounds during each batch of analysis conducted for each indoor environment: for homes, the LOD was 0.4 for benzene, 0.6 for limonene, 0.9 for toluene, 1.0 for octane, 1.1 for ethylbenzene and tetrachloroethylene, 1.2 for 1,2,4-trimethylbenzene, 1.3 for styrene, 1.6 for 2-ethylhexanol, and 1.9 for 2-phenoxyethanol; for schools: 0.3 for toluene, 0.4 for styrene, 0.7 for heptane, 0.8 for *o*-xylene, 0.9 for ethyl acetate, 1.2 for benzaldehyde and 2-butoxyethanol, 2.2 for 2-ethylhexanol, 2.3 for tetrachloroethylene, 1.6 for *m/p*-xylene, 2 for limonene, 1,2,4-Trimethylbenzene, ethylbenzene and butanol, 2.5 for α/β -pinenes and decane, 4.0 for naphthalene, 5.1 for 1-methoxy-2-propanol, and 5.3 for nonanal; and for swimming pools: 0.3 for bromodichloromethane, 0.4 for chloroform and bromoform, 0.5 for benzene, 0.6 for toluene and ethylbenzene, 0.7 for *p*-xylene, 0.8 for 1,2,4-trimethylbenzene, and 1.0 for dibromochloromethane. For the other identified compounds, the LOD was assumed to be the same as that obtained for toluene.

For the 3 studies, assessments were also always concurrently carried out outdoors.

2.3. Statistical Analyses and Study Assumptions

The indoor VOC concentrations reported in this work correspond to the average values obtained from the set of samples collected in each building. Data were organized by type of building (households, schools, and swimming pools), and the respective descriptive statistics were obtained using Microsoft Excel 2016. Values that were below the LOD of the method were treated as 0, and the detection frequency (DF)—defined as the proportion of measurements with values that exceeded the LOD—was calculated for each quantified VOC specie. To ascertain the relationship between indoor and outdoor concentrations, indoor-to-outdoor (I/O) concentration ratios were estimated for each individual VOC. Statistical analyses were performed using IBM SPSS Statistics (version 27). Data normality was assessed employing the Shapiro–Wilk test. Since the distribution of the study variables was skewed, nonparametric tests were applied. For the substances detected in the 3 indoor environments, differences in TVOC and individual VOC levels among households, schools, and swimming pools were tested using Kruskal–Wallis and Mann–Whitney *U* tests. For the Kruskal–Wallis test, the results are reported as the Kruskal–Wallis test value (*H*) representing the difference in mean rank numbers of more than two groups and by the degrees of freedom presented in parenthesis. In the case of Mann–Whitney *U* test, the results are reported as the *U* Mann–Whitney test value (*U*) that summarizes the difference in mean rank numbers of two groups, and by the respective standardized scores identified as *z*. Mann–Whitney *U* tests were also applied to determine the existence of statistically significant differences between TVOC concentrations measured indoors and the respective levels assessed in the outdoor environment. The existence of significant correlations was tested using the Spearman method, reported as r_s , for presenting the respective Spearman correlation coefficients.

3. Results and Discussion

TVOC concentrations found in this work varied, on average, from 29.6 to 791.2 $\mu\text{g}/\text{m}^3$ in homes, from 66.3 to 466.2 $\mu\text{g}/\text{m}^3$ in school buildings, and from 53.7 to 655.5 $\mu\text{g}/\text{m}^3$ in the indoor swimming pools surveyed. The mean TVOC levels indicated that households exhibited significantly greater fluctuations in chemical pollution compared to schools and swimming pools (Figure 1). In fact, the highest inter-building variation in TVOC levels was observed in homes. Moreover, 7% (2 out of 30) of the homes surveyed presented average TVOC concentrations exceeding the national limit value that has been established for commercial and service buildings (600 $\mu\text{g TVOC}/\text{m}^3$ [35]). For the sample of studied indoor swimming pools, only one facility presented average TVOC levels slightly higher than the national limit, whereas for schools, all the classrooms presented average TVOC concentrations below 600 $\mu\text{g}/\text{m}^3$. According to public information on IEQ guidelines worldwide [36], some countries, such as Belgium and Spain, set a strict limit value of 200 $\mu\text{g}/\text{m}^3$ for TVOCs in indoor environments. Based on this threshold, exceedances were observed in 63% of households, 50% of schools, and 30% of the surveyed swimming pools.

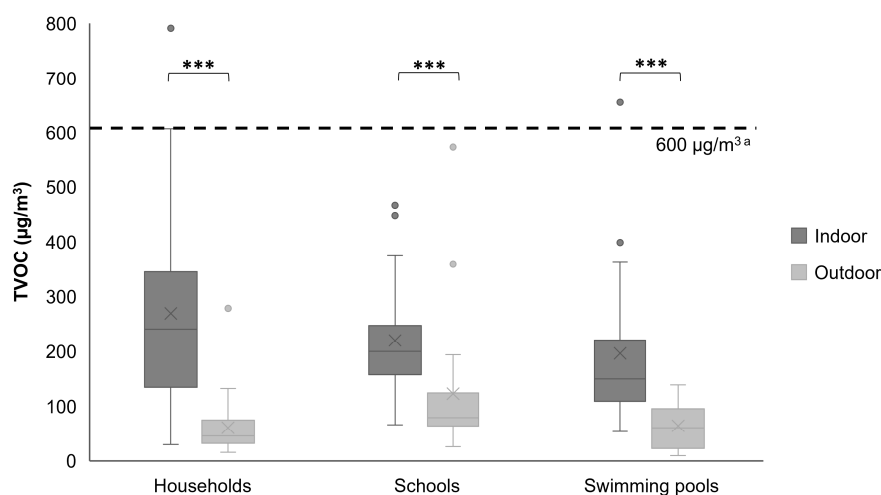


Figure 1. Boxplot representing airborne total volatile organic compound (TVOC) concentrations assessed in households ($n = 30$), schools ($n = 20$), and swimming pools ($n = 20$). The bottom and the top of the boxes represent the 25th and 75th percentiles, respectively. The band near the middle of the box and the X represent the median and the mean values, respectively. The ends of the whiskers indicate 10th and 90th percentiles. The dots located outside the boxes represent outliers. Asterisks show significant differences between the levels found indoors and in the respective outdoor environments, as determined by Wilcoxon tests ($*** p < 0.001$). The differences in TVOC concentrations across the three indoor settings are not statistically significant. ^a National recommended limit (Portaria n.º 138-G/2021, de 1 de julho [35]).

Noteworthy, although swimming pools have an important declared source of chemicals in indoor air—mainly related to the chlorinated water in the pool and its associated chemistry—the lowest mean TVOC concentrations were obtained in these settings compared to homes or schools. This may be related to specific building-related factors that are likely to contribute to a greater elimination/dilution rate of the chemicals produced indoors in the recreational facilities that were studied. These factors include the existence of heating, ventilation, and an air conditioning (HVAC) system; the typically greater volume of air due to the dimension of the indoor space; poorly insulated windows; and considerable air and/or water leakage in the building envelope (evident for some of the indoor swimming pools that were studied). Nevertheless, the statistical analysis of the TVOC concentrations measured across the indoor settings studied revealed no statistically significant differences.

When comparing the obtained TVOC levels (Figure 1 and Table 2) with those reported in previous global studies, we found the following:

- i) For homes, the levels were consistent with those reported for homes in the UK [37] and Greece [38], but were lower than those observed in other studies, such as Lee et al.'s research on atopic dermatitis patients in Seoul (mean: $648 \mu\text{g}/\text{m}^3$) [39] or the study of Mečiarová et al. involving Slovak households (apartments: $519.7 \mu\text{g}/\text{m}^3$; family houses: $330.2 \mu\text{g}/\text{m}^3$) [40];
- ii) For schools, the measured TVOC concentrations were significantly higher than those reported for mechanically ventilated classrooms in Finland and the USA ($<50 \mu\text{g}/\text{m}^3$) ($<50 \mu\text{g}/\text{m}^3$) [41,42], but the levels were in line with those observed in geographically neighboring countries, as observed in a study conducted in schools in the Mediterranean region of Spain [43];
- iii) For swimming pools, although the research on TVOC levels is limited, the concentrations found in this study were substantially higher than those reported for pool areas in similar facilities in Finland [44].

Table 2. Volatile organic compound concentrations measured in air samples collected from households, schools, and swimming pools.

	Location	Households (n = 30)				Schools (n = 20)				Swimming Pools (n = 20)			
		Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c
1,2,4-Trimethylbenzene	Indoor	2.0 (3.6)	16.9	12 (40.0)	20.0	2.3 (3.7)	16.3	16 (80.0)	4.6	0.4 (1.0)	3.9	6 (30.0)	>10 #
	Outdoor	0.1 (0.8)	4.1	1 (3.4)		0.5 (1.0)	3.0	5 (25.0)		n.d.	n.d.	n.d.	
1-Methoxy-2-propanol	Indoor	2.6 (7.7)	36.7	4 (13.3)	>10 #	13.1 (32.6)	142.5	8 (40.0)	0.7	1.7 (3.2)	12.6	8 (40.0)	0.6
	Outdoor	n.d.	n.d.	n.d.		19.8 (86.7)	388.0	2 (10.0)		3.0 (13.5)	60.2	1 (5.0)	
2,2,4,4,6,8,8-Heptamethylnonane	Indoor	4.9 (18.2)	97.2	6 (20.0)	16.3	n.d.	n.d.	n.d.	n.a.	0.8 (1.6)	4.8	4 (20.0)	>10 #
	Outdoor	0.3 (1.4)	7.5	1 (3.4)		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
2-Butoxyethanol	Indoor	n.d.	n.d.	n.d.	n.a.	8.1 (21.7)	83.3	5 (25.0)	0.7	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		11.7 (51.4)	229.9	2 (10.0)		n.d.	n.d.	n.d.	
2-Ethylhexanol	Indoor	1.4 (2.7)	9.1	8 (26.7)	2.8	4.0 (4.9)	19.9	15 (75.0)	1.5	1.2 (2.7)	11.7	10 (50.0)	2.4
	Outdoor	0.5 (2.0)	8.5	2 (6.9)		2.6 (9.8)	43.8	4 (20.0)		0.5 (1.3)	4.2	3 (15.0)	
2-Methylbutanenitrile	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	6.9 (4.5)	19.9	19 (95.0)	>10 #
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
2-Phenoxyethanol	Indoor	1.1 (2.5)	9.8	5 (16.7)	2.8	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	0.4 (1.9)	10.2	1 (3.4)		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
3-Carene	Indoor	1.7 (4.7)	24.3	7 (23.3)	>10 #	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
3-Methylbutanenitrile	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	7.5 (5.7)	26.0	19 (95.0)	>10 #
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Acetic acid	Indoor	3.9 (9.6)	37.4	5 (16.7)	>10 #	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Acetophenone	Indoor	1.6 (2.1)	7.6	14 (46.7)	0.5	1.1 (1.3)	3.5	10 (50.0)	0.6	0.2 (0.4)	1.3	6 (30.0)	>10 #
	Outdoor	3.0 (4.4)	21.7	16 (55.2)		1.8 (2.2)	7.5	10 (50.0)		n.d.	n.d.	n.d.	
Benzaldehyde	Indoor	4.8 (3.7)	16.2	26 (86.7)	0.7	11.4 (7.2)	27.7	20 (100)	0.7	4.6 (2.7)	12.8	20 (100)	2.3
	Outdoor	7.3 (6.9)	32.3	25 (86.2)		15.8 (9.5)	44.3	19 (95.0)		2.0 (1.6)	5.9	16 (80.0)	
Benzene	Indoor	1.2 (1.1)	4.6	20 (66.7)	0.7	0.9 (0.6)	2.4	20 (100)	0.8	0.5 (0.8)	3.5	9 (45.0)	1.3
	Outdoor	1.7 (1.4)	5.0	22 (75.9)		1.1 (0.7)	2.4	19 (95.0)		0.4 (0.8)	2.7	6 (30.0)	
Benzonitrile	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	1.3 (1.6)	6.3	13 (65.0)	>10 #
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Benzyl acetate	Indoor	0.6 (1.6)	5.5	5 (16.7)	>10 #	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
BHT, butylated hydroxytoluene	Indoor	n.d.	n.d.	n.d.	n.a.	0.8 (2.1)	8.4	4 (20.0)	>10 #	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Butanol	Indoor	1.6 (4.7)	24.2	6 (20.0)	>10 #	2.0 (2.7)	7.8	9 (45.0)	6.7	0.6 (0.9)	2.7	9 (45.0)	0.5
	Outdoor	n.d.	n.d.	n.d.		0.3 (0.9)	2.9	2 (10.0)		1.3 (2.8)	9.6	4 (20.0)	

Table 2. Cont.

	Location	Households (n = 30)				Schools (n = 20)				Swimming Pools (n = 20)			
		Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c
Butyl acetate	Indoor	3.0 (8.8)	36.9	4 (13.3)	>10 [#]	n.d.	n.d.	n.d.	n.a.	2.0 (2.2)	7.6	13 (65.0)	0.9
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	2.3 (4.2)	13.5	
Cyclohexanone	Indoor	n.d.	n.d.	n.d.	n.a.	1.0 (3.0)	10.8	2 (10.0)	>10 [#]	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Decamethylcyclopentasiloxane	Indoor	63.5 (128.2)	611.5	11 (36.7)	14.4	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	4.4 (23.6)	127.3	1 (3.4)		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Decanal	Indoor	1.4 (1.8)	5.8	14 (46.7)	2.3	1.0 (1.3)	3.3	8 (40.0)	1.4	3.1 (1.9)	6.9	19 (95.0)	0.3
	Outdoor	0.6 (1.5)	5.3	5 (17.2)		0.7 (1.4)	4.9	5 (25.0)		10.2 (9.0)	31.1	19 (95.0)	
Decane	Indoor	2.5 (5.5)	22.1	8 (26.7)	12.5	1.7 (2.2)	8.1	10 (50.0)	5.7	n.d.	n.d.	n.d.	n.a.
	Outdoor	0.2 (0.9)	5.0	1 (3.4)		0.3 (0.9)	3.1	3 (15.0)		n.d.	n.d.	n.d.	
Dichloroacetonitrile	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	8.9 (6.4)	25.4	19 (95.0)	>10 [#]
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Ethyl acetate	Indoor	8.6 (23.6)	114.5	11 (36.7)	86.0	25.4 (39.6)	163.8	17 (85.0)	9.1	0.3 (0.6)	2.6	6 (30.0)	0.5
	Outdoor	0.1 (0.6)	2.9	2 (6.9)		2.8 (5.1)	21.8	9 (45.0)		0.6 (1.6)	5.1	3 (15.0)	
Ethylbenzene	Indoor	1.8 (3.2)	12.9	12 (40.0)	9.0	2.7 (4.4)	19.9	17 (85.0)	3.4	1.8 (3.6)	16.2	16 (80.0)	2.0
	Outdoor	0.2 (0.7)	3.5	3 (10.3)		0.8 (0.9)	2.4	11 (55.0)		0.9 (1.4)	4.1	7 (35.0)	
Heptane	Indoor	n.d.	n.d.	n.d.	n.a.	2.0 (2.9)	9.9	9 (45.0)	6.7	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		0.3 (1.0)	3.4	2 (10.0)		n.d.	n.d.	n.d.	
Hexanal	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	0.7 (1.4)	6.0	6 (30.0)	0.5
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		1.4 (2.6)	8.6	5 (25.0)	
Hexane	Indoor	n.d.	n.d.	n.d.	n.a.	20.5 (77.8)	346.4	3 (15.0)	>10 [#]	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Hexanoic acid	Indoor	n.d.	n.d.	n.d.	n.a.	1.1 (2.7)	10.3	4 (20.0)	11.0	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		0.1 (0.4)	1.8	1 (5.0)		n.d.	n.d.	n.d.	
Isobutyronitrile	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	6.1 (7.9)	36.5	18 (90.0)	>10 [#]
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Limonene	Indoor	18.2 (22.5)	90.4	26 (86.7)	20.2	23.2 (24.8)	111.6	20 (100)	16.6	1.6 (1.8)	6.4	17 (85.0)	3.2
	Outdoor	0.9 (3.9)	21.1	3 (10.3)		1.4 (4.8)	21.6	4 (20.0)		0.5 (1.0)	3.6	4 (20.0)	
m/o/p-Xylenes	Indoor	15.4 (18.4)	85.2	28 (93.3)	4.2	13.7 (19.6)	81.1	19 (95.0)	2.5	6.4 (10.2)	45.7	19 (95.0)	1.9
	Outdoor	3.7 (4.4)	21.0	22 (75.9)		5.4 (5.2)	24.9	18 (90.0)		3.4 (4.3)	13.7	12 (60.0)	
Methylcyclohexane	Indoor	n.d.	n.d.	n.d.	n.a.	1.1 (1.3)	3.4	10 (50.0)	>10 [#]	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Naphthalene	Indoor	0.2 (0.4)	1.8	4 (13.3)	>10 [#]	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Nonanal	Indoor	3.4 (3.2)	9.7	18 (60.0)	5.7	4.7 (4.7)	18.0	14 (70.0)	3.6	1.8 (1.3)	5.1	18 (90.0)	0.2
	Outdoor	0.6 (1.5)	6.8	5 (17.2)		1.3 (2.3)	9.3	7 (35.0)		7.3 (5.8)	20.5	18 (90.0)	

Table 2. Cont.

	Location	Households (n = 30)				Schools (n = 20)				Swimming Pools (n = 20)			
		Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c	Mean (SD) ^a	Max ^a	n (DF) ^b	I/O ^c
Nonane	Indoor	0.7 (2.0)	7.3	3 (10.0)	>10 #	0.2 (0.5)	1.7	5 (25.0)	>10 #	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Octanal	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	0.4 (0.7)	2.2	7 (35.0)	0.3
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	1.4 (2.0)	5.6	
Octane	Indoor	1.1 (2.9)	12.0	5 (16.7)	5.5	0.8 (1.8)	5.3	4 (20.0)	4.0	n.d.	n.d.	n.d.	n.a.
	Outdoor	0.2 (1.3)	6.9	1 (3.4)		0.2 (0.8)	3.6	1 (5.0)		n.d.	n.d.	n.d.	
Phenol	Indoor	n.d.	n.d.	n.d.	n.a.	1.2 (2.0)	5.8	7 (35.0)	0.5	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		2.3 (3.6)	11.1	7 (35.0)		n.d.	n.d.	n.d.	
Phthalic anhydride	Indoor	n.d.	n.d.	n.d.	n.a.	0.7 (1.4)	4.9	6 (30.0)	0.8	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		0.9 (2.5)	10.4	4 (20.0)		n.d.	n.d.	n.d.	
Styrene	Indoor	1.0 (3.5)	18.1	7 (23.3)	10.0	0.8 (0.8)	3.0	18 (90.0)	0.6	0.5 (0.7)	3.1	12 (60.0)	2.5
	Outdoor	0.1 (0.2)	0.8	3 (10.3)		1.4 (4.6)	20.9	15 (75.0)		0.2 (0.4)	1.2	3 (15.0)	
Tetrachloroethylene	Indoor	0.3 (1.0)	3.9	4 (13.3)	3.0	0.4 (0.9)	3.6	3 (15.0)	0.5	0.4 (0.7)	2.2	7 (35.0)	4.0
	Outdoor	0.1 (0.5)	2.8	2 (6.9)		0.8 (3.6)	16.3	1 (5.0)		0.1 (0.4)	1.4	2 (10.0)	
Tetradecane	Indoor	0.2 (0.8)	4.1	3 (10.0)	>10 #	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
Tetrahydrofuran	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	1.6 (2.9)	9.9	8 (40.0)	0.3
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		5.1 (18.7)	84.0	4 (20.0)	
Toluene	Indoor	15.5 (18.1)	79.6	29 (96.7)	3.3	14.5 (13.7)	64.7	20 (100)	2.4	7.6 (7.8)	27.8	19 (95.0)	1.4
	Outdoor	4.7 (4.3)	21.7	26 (89.7)		6.1 (7.4)	36.0	19 (95.0)		5.4 (5.9)	22.5	16 (80.0)	
Undecane	Indoor	1.3 (4.1)	19.8	4 (13.3)	>10 #	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	
α/β -Pinenes	Indoor	8.6 (9.3)	42.0	25 (83.3)	14.3	1.5 (2.2)	8.6	11 (55.0)	3.8	n.d.	n.d.	n.d.	n.a.
	Outdoor	0.6 (2.8)	15.1	2 (6.9)		0.4 (1.2)	3.9	3 (15.0)		n.d.	n.d.	n.d.	
TTHM	Indoor	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.	n.d.	n.a.	95.4 (117.8)	563.3	20 (100)	63.6
	Outdoor	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.		1.5 (3.1)	8.6	5 (25.0)	
TVOC	Indoor	269.3 (177.3)	791.2	30 (100)	4.4	219.9 (112.9)	466.2	20 (100)	1.8	196.0 (141.0)	655.5	20 (100)	3.0
	Outdoor	60.6 (50.9)	278.4	29 (100)		122.8 (129.5)	573.5	20 (100)		64.3 (42.4)	139.0	20 (100)	

DF, detection frequency; I/O: indoor-to-outdoor concentration ratio; Max, maximum; n.a., not applicable; n.d., not detected, represented values lower than limit of detection described in Section 2.2; SD, standard deviation; TTHM, total trihalomethanes (chloroform, bromoform, bromodichloromethane, and dibromochloromethane); TVOCs, total volatile organic compounds. ^a Values are presented in $\mu\text{g}/\text{m}^3$. ^b n corresponds to the number of samples with concentrations above the limit of detection and DF to the detection frequency, in percentage, considering the total number of samples. ^c I/O ratios of individual VOCs are calculated using the mean concentration obtained in each sampling location. # Substances exclusively detected indoors are considered as having a percentage of detection higher than 10.

TVOC concentration is widely regarded as a proxy for chemical pollution load and/or an indicator of the existence of conditions that may favor the accumulation of chemicals in indoor air (e.g., due to poor ventilation). Nevertheless, a poor link between exposure to TVOC concentrations and health effects has also been documented [45]. In fact, the characteristics of the individual substances existing in the environmental mixture, including the respective relative concentrations and physical, chemical, and toxicological properties, are expected to more accurately define the biological response to chemical pollution [46]. For this reason, this study also included the analysis of the individual VOCs detected in the samples collected in the three indoor environments. The substances showing a percentage of detection higher than 10 in at least one of the indoor environments are listed in Table 2.

Interestingly, considering this criterion ($DF > 10$), a very similar number of substances was quantified in the sampled homes ($n_{\text{individual VOC}} = 30$), schools ($n_{\text{individual VOC}} = 29$), and indoor swimming pools ($n_{\text{individual VOC}} = 30$). A total of 16 individual VOCs, including aromatic hydrocarbons (1,2,4-trimethylbenzene, benzene, ethylbenzene, m/o/p-xylenes, styrene, and toluene), chlorinated hydrocarbons (tetrachloroethylene), alcohols (2-ethylhexanol and butanol), aromatic ketones (acetophenone), esters (ethyl acetate), aldehydes (benzaldehyde, decanal, nonanal), glycol ethers (1-methoxy-2-propanol), and terpenes (limonene), were quantified in all of the three indoor environments surveyed. This result suggests that the combined exposure to these 16 substances is very likely to occur and, thus, indoor air typically found in homes, classrooms, and swimming pools can contribute to the overall exposure of children to these hazardous chemicals. In fact, growing evidence indicates relevant associations between combined exposure to so-called chemical families (including VOCs) and their health effects [47]. Consequently, the additive or synergistic effects—resulting in increased health risks—resulting from combined exposure to these 16 substances in homes, schools, and recreational environments, such as swimming pools, cannot be excluded. This should be taken in consideration in further risk assessment studies.

The investigation of the existence of statistically significant differences among the individual VOC concentrations assessed in the three environments revealed that exposure to some of these substances can be particularly potentiated in a given indoor setting due to the observation of significantly greater concentrations. Specifically, classrooms presented significantly higher levels of 2-ethylhexanol ($H(2) = 11.23$, $p = 0.004$), benzaldehyde ($H(2) = 14.14$, $p < 0.001$), and ethyl acetate ($H(2) = 21.58$, $p < 0.001$) than households and indoor swimming pools. In addition, levels of 1,2,4-trimethylbenzene ($H(2) = 9.02$, $p = 0.011$) were similar to those found in homes, but significantly higher in schools than those assessed in indoor swimming pools. In turn, indoor swimming pools presented significantly lower levels of benzene ($H(2) = 10.02$, $p = 0.007$) and limonene ($H(2) = 27.33$, $p < 0.001$) and significantly higher levels of decanal ($H(2) = 15.30$, $p < 0.001$) than households and schools. The boxplots for representing the concentration levels for the substances that showed significant differences across the different microenvironments are presented in Figure S2 in the Supplementary Materials.

Recently, the WHO published a list of 17 critical chemicals to be considered when assessing exposure to multiple chemicals in educational settings for children [15]. Ten out of the 13 VOCs that are on the WHO list were among the individual VOCs identified in this study. In particular, benzene, ethylbenzene, xylenes (o,m,p), styrene, toluene, limonene, and tetrachloroethylene were not only detected in samples collected in schools, but also in homes and swimming pools. Importantly, some of these compounds (benzene, xylenes, styrene, and toluene) were found, on average, at higher concentrations in the indoor air of households than in classrooms (Table 2). In turn, butyl acetate and naphthalene were not detected at appreciable concentrations (and % of detection) in the sample of schools surveyed in this study, but these substances were, for instance, detected in at least one of the other indoor settings studied.

Concurrent sampling of airborne VOCs indoors and outdoors in all surveyed buildings allowed us to explore statistically significant correlations between indoor and outdoor

TVOC levels and also to calculate the average I/O concentration ratio for each substance. This is expected to provide information on the real contribution of ambient air pollution and of sources located indoors to the overall chemical air pollution found in the surveyed buildings. On average, the indoor TVOC concentrations were only significantly and positively correlated to the TVOCs assessed in the outdoor environment of school buildings (homes: $r_s = 0.19$, $p = 0.326$; schools: $r_s = 0.45$, $p = 0.049$; swimming pools: $r_s = 0.12$, $p = 0.613$). Nevertheless, indoor TVOC concentrations were significantly higher than those measured outdoors for all three types of buildings surveyed (homes: $U = 74.00$, $z = -5.47$, $p < 0.001$; schools: $U = 75.00$, $z = -3.38$, $p < 0.001$; swimming pools: $U = 48.00$, $z = -4.11$, $p < 0.001$, Figure 1). In fact, from the analysis of the I/O concentration ratio obtained for individual VOCs, the results show evidence of emissions from indoor sources. 1,2,4-trimethylbenzene showed substantially high I/O concentration ratios in all three microenvironments (homes: I/O = 20.0; schools: I/O = 4.6; and swimming pools: I/O > 10.0) (Table 2). This suggests that emissions originate from indoor sources that can be common to the three indoor microenvironments. Additionally, 2-ethylhexanol, ethylbenzene, limonene, m/o/p-xylenes, and toluene were also found at mean I/O concentration ratios that exceeded the levels in homes, schools, and swimming pools. Thus, these substances are likely to receive contributions from emissions produced from both indoor and outdoor sources in the three indoor microenvironments, with indoor sources having an apparent higher influence. Most of these substances are of toxicological concern and are reported as being common components of putative indoor sources, such as adhesives and sealants, anti-freeze products, biocides (e.g., disinfectants and pest control products), coating products, fillers, putties, plasters, modeling clay, finger paints, non-metal-surface treatment products, inks and toners, leather treatment products, lubricants and greases, polishes and waxes, textile treatment products, and detergents [48,49].

Furthermore, from the panel of VOCs listed in Table 2, some substances seem to be more specific to a particular indoor environment. For instance, 2-phenoxyethanol, 3-carene, acetic acid, benzyl acetate, decamethylcyclopentasiloxane, naphthalene, tetradecane, and undecane were only detected at quantifiable levels in households. With the exception of 2-phenoxyethanol, all the other individual VOCs were found to apparently primarily originate from indoor sources (I/O concentration ratio > 10). In fact, most of these substances are common components of indoor sources that are very likely to exist in households, including machine wash liquids/detergents, household cleaning products, personal care products, paints and coating or adhesives, fragrances, and air fresheners [48,49]. Noteworthy, for homes, the cyclic siloxane D5 (decamethylcyclopentasiloxane) was identified as the VOC with the highest maximum concentration indoors. In 2018, D5 was recognized as persistent, bioaccumulative, and toxic (PBT), leading to its classification as a candidate Substance of Very High Concern (SVHC) by the REACH regulation [50]. This classification prompted the publication of Commission Regulation (EU) 2024/1328, which introduced restrictions on the use of D5 and also of Octamethylcyclotetrasiloxane (D4) and Dodecamethylcyclohexasiloxane (D6) [51]. The new regulation seeks to reduce environmental risks associated with these chemicals, particularly in leave-on cosmetic products, where their widespread use significantly contributes to environmental contamination, as highlighted by the findings of this study. With the new regulation, D4 and D5 are restricted in concentrations equal to or greater than 0.1% by weight in final products, effective from June 2026. However, deferral periods are provided for certain uses, such as medical devices and dry-cleaning solvents, to provide industries time to adapt and transition to safer alternatives. Interestingly, the D5 concentrations obtained in this study were in line with those reported in previous studies conducted in European countries geographically close to Portugal (such as Spain (23–293 $\mu\text{g}/\text{m}^3$ [52]), Italy (38–170 $\mu\text{g}/\text{m}^3$), and the UK 45–150 $\mu\text{g}/\text{m}^3$ [53]), but considerably higher than those reported in studies from more distant geographic areas (USA: 18–812 ng/m^3 [54]; Vietnam (<LOD–600 ng/m^3) [55]). Differences in D5 exposure across regions are likely influenced by variations in consumption patterns, including the types and quantities of cosmetic products. Additionally, factors such as product regu-

lations, local climate conditions, and quality of home ventilation practices may further contribute to the variability in indoor concentrations of D5. If the new regulation is effectively implemented, exposure to D5 is expected to decrease significantly starting in 2026, particularly across the EU. However, further studies will be necessary to assess the effectiveness of this implementation and to monitor its impact on exposure levels over time. 2-butoxyethanol, BHT (butylated hydroxytoluene), cyclohexanone, heptane, hexane, hexanoic acid, methylcyclohexane, phenol, and phthalic anhydride were the individual VOCs that were exclusively found in classrooms. All these substances, except heptane, were found at I/O concentration ratios that exceeded 10, and thus apparently primarily originated from sources existing inside the school buildings. In fact, in our past study, we found that some of these substances were significantly correlated with characteristics of classrooms, including the use of cleaning products with ammonia (BHT, phenol, and phthalic anhydride) and indoor pesticides for rodents, cockroaches, and/or ants (hexane) [29]. Moreover, heptane, phenol, and phthalic anhydride were found to be also significantly correlated with the density of occupancy in the classrooms [29]. The school environment was the only setting where the VOCs present at higher concentrations (ethyl acetate) were not exclusively detected in this indoor environment. However, the levels of ethyl acetate found in classrooms were 3- and 76-fold higher than the concentrations observed in homes and swimming pools. Interestingly, the concentration of ethyl acetate found in this study was considerably higher than that reported in previous studies [56,57]. In particular, a study conducted in a primary school in China also identified ethyl acetate among the top-15 detected substances, attributing its presence to emissions from nearby industrial sources and the evaporation of solvents [56]. However, industrial sources are unlikely to account for the ethyl acetate levels observed in our study, as only one of the schools surveyed was located in a mixed industrial/residential area, where the concentration of ethyl acetate was $17 \mu\text{g}/\text{m}^3$. In contrast, the majority of the schools (85%) were situated in urban centers with densely packed housing or in town areas with small gardens. Given that ethyl acetate is a commonly used solvent in products such as paints, varnishes, lacquers, cleaning agents, and perfumes, it is reasonable to assume that solvent evaporation from these products within the schools may explain the detected concentrations. For instance, a study examining various classrooms in a vocational training school found that ethanol and ethyl acetate were the most frequently detected solvents in artistic make-up and cosmetology classrooms [58]. While this study did not gather detailed information on the specific products used in the schools, definitive conclusions about the sources of ethyl acetate cannot be drawn.

As expected, for swimming pools, disinfection by-products (DBPs) belonging to the chemical family of trihalomethanes (THMs, including chloroform, bromoform, bromodichloromethane, and dibromochloromethane) were the predominant compounds found indoors. The sum of THM concentrations observed are consistent with the range reported in previous studies [59]. Additionally, in line with the data from similar facilities across Europe [59,60], chloroform was the VOC/THM present at the highest concentrations, with average levels ranging from below the LOD to $352 \mu\text{g}/\text{m}^3$ in the assessed swimming pool facilities. The average chloroform concentration obtained in this study ($66 \mu\text{g}/\text{m}^3$) was slightly higher than that reported in previous studies [60,61] (11 and $54.50 \mu\text{g}/\text{m}^3$). The elevated levels observed here can be attributed to the sampling locations that included areas both immediately above the pool water surface and within the immediate vicinity of the pool. In contrast, most prior studies have primarily focused on air quality within the swimming pool environment itself, often neglecting the real exposure of individuals during active swimming activities. This study's focus on the breathing zone of swimmers, considering both periods in which they are conducting activities in the water and resting in the vicinity of the pool is likely to provide a more accurate assessment of real-world exposure. In fact, as noted in our previous publication [30], we observed statistically significant higher concentrations of THM in samples collected near the water's surface, further supporting the notion that these elevated chloroform levels are more representative of real exposure during swimming activities. In addition to THM, dichloroacetonitrile, 2-

methylbutanenitrile, 3-methylbutanenitrile, benzonitrile, hexanal, isobutyronitrile, octanal, and tetrahydrofuran were the VOCs detected in indoor swimming pools, but not in homes or schools. Hexanal, octanal, and tetrahydrofuran were found at I/O concentration ratios lower than the unity, suggesting that their nature is related to emissions from sources located in the outdoor environment in the surroundings of the indoor environments studied. All the remaining substances (including THM, dichloroacetonitrile (other DBPs belonging to the family of haloacetonitrile), and other nitriles) seem to originate from indoor sources (I/O concentration ratio > 10), linked to the characteristic chemistry of the disinfection of swimming pool water to prevent waterborne diseases [62].

The environmental concentrations of air contaminants that co-exist in each indoor environment may or may not be correlated to one another. In this study, we found that some of the identified substances had concentrations that significantly correlated with the levels of other chemical species that were concomitantly assessed (Tables S1–S3 in the Supplementary Materials). In particular, some significant and positive correlations were observed in all the three indoor environments studied (concentrations of 1,2,4-trimethylbenzene with ethylbenzene and xylenes levels; ethylbenzene with benzene, m,o,p-xylenes and toluene; m,o,p-xylenes with toluene; acetophenone with benzaldehyde; and decanal with nonanal). Indeed, many air pollutants might have interrelated natures, which explains their frequent co-occurrence in indoor air. A correlation between environmental contaminant concentrations may indicate that these substances share common source(s).

4. Study Strengths and Limitations

The novelty of this study is the use of a robust database, enabling a comprehensive and integrated analysis across VOC concentration levels obtained in multiple settings, which provide valuable scientific insights and contribute to expanding our knowledge on a topic with recognized limited existing data. Unlike typical studies, which are conducted separately and in isolation, this approach combined data from the same laboratory using consistent analytical methods, uncovering findings that are more informative and impactful than the sum of individual studies. Indeed, the exploration of available data is crucial for defining future research priorities for properly understanding the exposome. In particular, this study presents the concentrations of multiple VOCs to which children are exposed in living, educational, and recreational environments in the same geographical area, providing valuable evidence for designing further risk assessment studies considering the cumulative exposure to several stressors. Nevertheless, in addition to pollutant levels, information on other determining aspects, such as the timing, duration, and frequency of contact with pollutants, needs to be considered in the models to accurately estimate exposure and respective risks to health.

The results presented in this work are representative of the indoor air conditions of the studied buildings, namely at the time the assessments were conducted. Significant efforts were made to implement QA/QS procedures to guarantee the quality of the data within each study by following harmonized methodological approaches and by carrying out all the analyses in the same laboratory. Nevertheless, some study limitations related to the differential characteristics of the design of the protocol that was followed in the three studies need to be considered. Namely, the IAQ assessment plans conducted in homes, schools, and swimming pools were not concurrent. Thus, the possibility of the introduction of some degree of uncertainty in the findings resulting from the comparison of concentrations found in the different studies cannot be disregarded. The criteria for seasonal variation were also different in the three studies. For households, the results were obtained from one campaign independently of the season (10 dwellings were audited in the warm and 20 in the cold season); in schools, all concentrations reported were obtained during the cold season (similarly to the SINPHONIE EC project [63]). In swimming pools, season fluctuations were taken into consideration, with two sampling campaigns conducted in different seasons. This is very likely to impact differently the representativeness of the reported concentrations for the indoor air conditions verified in the whole year. In addition,

it is important to note that the analytical methodologies employed in the study only covered part of the potentially relevant hazardous substances. For example, specific chemicals, such as chloramines, which can constitute an important fraction of airborne chemical pollution in the indoor environment of indoor swimming pools were not measured in this study. Furthermore, since concentrations below the LOD were treated as zero in the calculations, an eventual underestimation of the amount of some of the reported VOCs cannot be excluded.

5. Conclusions

Evidence shows that VOC concentrations to which children are exposed in the several indoor environments, such as home, schools, and swimming pools, are consistently higher than those detected in the ambient air surroundings of the analyzed buildings. In particular, this work also provided evidence that children are likely to be co-exposed to a common mixture of 16 VOCs in living, educational, and recreational indoor environments. For instance, most of the chemicals found in the study seem to be mainly attributed to emissions resulting from indoor sources, such building materials and detergents. Thus, more stringent source control strategies (e.g., selection of certified low-emitting materials) can be paramount for reducing exposure to a mixture of chemicals in the generality of buildings.

In particular, according to the specific VOCs detected in homes, emissions from the use of household cleaning products, personal care products, and fragranced consumer products, such as air fresheners, are likely to have an important contribution to the chemical pollution load in domestic environments. This is a key result, as policies and awareness campaigns might have a large impact by informing households about the contributions of fragranced consumer products to overall indoor emissions and recommendations on their use (e.g., use only in indoor spaces that are well ventilated) to reduce exposure in residential buildings. In the same spirit, for schools, the substitution of cleaning products with ammonia and a reduction in the number of pupils per classroom could lead to a reduction in concentrations of specific VOCs in the classroom environment.

In summary, the findings from this work support the need for further studies to extend the knowledge of the risk that combined exposure to multiple chemicals of indoor air can represent for children. Further research should consider an investigation of the combined effects of the mixture of substances in indoor air and the duration and frequency of exposure in different microenvironments.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos15121471/s1>, Figure S1. Location of surveyed homes, schools, and indoor swimming pools in Northern Portugal (Southern Europe) (source: Google Earth, 2021); Table S1. Spearman correlation coefficients between individual VOCs detected in the 30 households; Table S2. Spearman correlation coefficients between individual VOCs detected in the 20 schools; Table S3. Spearman correlation coefficients between individual VOCs detected in the 20 swimming pools.

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