

Estimation of Total VOC Emission and Ozone Removal Rates in a Primary School Classroom

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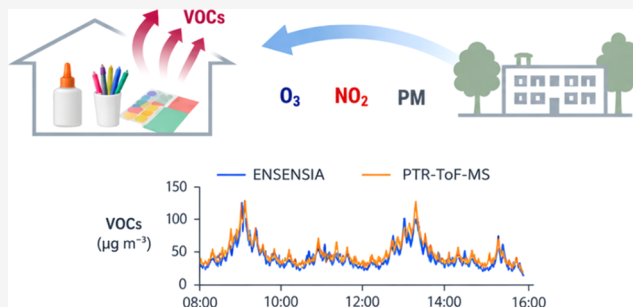
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ABSTRACT: Measurements of gaseous and particulate pollutants were conducted inside and outside a classroom in an urban area of Athens, Greece, using both reference instruments and low cost sensors. These data were used to evaluate indoor air quality and to estimate the emissions of total volatile organic compounds (VOCs) inside the classroom. The average air exchange rate during classes was estimated at 6.4 h^{-1} , based on the CO_2 concentration measurements. Paints, craft materials, and cleaning products have been identified as major indoor sources of VOCs. Total VOC emission rates varied depending on the type of class activities, with an average value of 1.3 mg min^{-1} during classes. Emitted VOCs included formaldehyde, acetaldehyde, acetone, methanol, ethanol, C8–C9 aromatics, etc. A classroom indoor air quality model reproduced the observed indoor concentrations of carbon monoxide, nitrogen dioxide, and fine particulate matter, assuming that outdoor sources were the only source of these pollutants. The average ozone removal rate constant was estimated at 10 h^{-1} during classes.

KEYWORDS: *in-classroom air quality, ozone removal, VOC emission rate, air change rates*



INTRODUCTION

Indoor air quality (IAQ) is associated with mental and physical health.^{1–3} Children are especially vulnerable to poor IAQ due to their higher respiratory rates, which can lead to increased incidences of asthma, reduced academic performance, and impaired cognitive development. Depending on the season and the country, air quality in classrooms is greatly influenced by the ventilation practices.^{4–8} Efficient ventilation has been associated with low pollutant levels and compliance with World Health Organization (WHO) air quality guidelines.^{7,9–11}

Pollutants that are typically associated with IAQ are carbon monoxide (CO), nitrogen oxides (NO_x), ozone (O_3), volatile organic compounds (VOCs), and particulates, specifically particles with diameter less than 1 or $2.5 \mu\text{m}$ (PM_1 and $\text{PM}_{2.5}$).^{8,12–17} In classrooms, VOCs are typically emitted by arts and crafts activities, cleaning products, carpets, and humans.^{18–21} Elevated levels of VOCs and/or prolonged exposure have been associated with respiratory and cardiovascular inflammation, cellular damage, and impacts on the nervous system.^{7,8} The winter period is typically of high interest, as low outdoor temperatures typically limit natural ventilation through window opening, leading to pollutant accumulation indoors. However, prevention of pollutant accumulation can be achieved by efficient ventilation.^{8,10,22}

The high cost and potential difficulty in transporting high-end instrumentation in school units raise the need for lower cost instrumentation that would not disrupt school settings. The use of low-cost sensors could assist in estimating pollutant levels in school classrooms. Measurements using online and offline high-end instrumentation and low-cost sensors have been conducted in different schools across different countries.^{8,16,17,22–27} At the same time, simple models can help in the estimation of the corresponding pollutant emission levels. Previous studies have developed models providing estimates of the air exchange rate and the indoor particulate levels in school classrooms.^{28,29} Kolokotroni et al. (2002) used a multizone approach, separating the classroom in zones and estimating for each case the ventilation rate.²⁸ These approaches provide valuable information; however, they have usually focused on ventilation rate and indoor particle concentration.

Measurements of in-classroom VOCs have reported concentrations of 2.8–9.5 ppb for acetaldehyde during winter

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in Athens, Greece, 1–3.5 ppb for benzaldehyde during winter in Italy, 0.03–3.5 ppb for benzene during winter in California, USA, 0.03–75 ppb for toluene during winter in China, 0.2–1 ppb for styrene during winter in France, 0.1–1.5 ppb for C9 aromatics during winter in Greece, and 1–30 ppb for total VOCs classrooms around the world.^{8,22,26,30–33} Indoor CO, NO₂, and fine particulate matter levels in schools are often dominated by outdoor air infiltration.²² Reported indoor NO₂ levels in European schools typically range between 3 and 38 ppb.¹⁷ PM_{2.5} levels in classrooms range between 10 and 30 $\mu\text{g m}^{-3}$.^{17,22,34} Studies in schools in Athens, Greece, reported average indoor PM_{2.5} concentrations of 15 $\mu\text{g m}^{-3}$ and NO₂ levels of 6 ppb.³⁵

O₃ in classrooms is typically of outdoor origin.^{36,37} O₃ is a secondary pollutant formed via photochemical reactions involving NO_x and VOCs. The main sources of these precursors in an urban environment are motor vehicle exhaust, industrial combustion, power generation, and biogenic sources including vegetation.³⁸ Photolysis of NO₂ initiates O₃ formation, while VOC oxidation sustains its production via conversion of NO to NO₂, resulting in increased O₃ levels in urban areas.^{38,39} Inside classrooms, usually, there are no significant O₃ sources, such as printing machines or O₃ producing air cleaners. Thus, the indoor O₃ concentrations are determined by the balance between outdoor supply and indoor removal processes. Surfaces that act as O₃ sinks are in abundance indoors.^{40–42} Fischer et al. (2013) reported an average O₃ removal rate constant in an occupied classroom of 0.1 h^{−1} per 11 year old pupil.⁴³ They estimated that the ozone removal due to the presence of the 24 students and their teacher was 2.5 times higher than that for the removal on the surfaces in the classroom. Wisthaler and Weschler (2010) reported an average removal rate of 0.9 h^{−1} per adult attributed specifically to reactions between ozone and human skin lipids.⁴⁴ Their value was obtained under controlled conditions designed to isolate the contribution of human emissions and surface chemistry associated with skin lipids. Part of the difference between the two reported rate constants is due to the different conditions of the two studies (children versus adults, classroom versus a controlled laboratory environment), but part of it is also due to the variability of the corresponding chemical and physical processes involved in O₃ removal. The quantification of O₃ removal rates inside classrooms is essential for estimation of indoor O₃ levels.

In the present work, the emissions of total VOCs and the O₃ removal rates are estimated combining classroom measurements with a box model. The rates are calculated during school operation (classes and breaks) and nonschool hours. The model's performance is evaluated using both the reference instruments and the low-cost sensor inputs. The sources of other pollutants including CO, NO₂, and fine PM are also investigated.

EXPERIMENTAL METHODS

Campaign Overview

The eighth Zografou primary school, located near the city center of the capital of Greece, Athens, was used for the measurements. It was part of the investigation of air quality in school classrooms within the scope of the European program "Disrupting Noxious Synergies of Indoor Air Pollutants and their Impact in Childhood Health and Wellbeing, using Advanced Intelligent Multisensing and Green Interventions (SynAir-G)".⁴⁵ The school is surrounded by residential buildings and is adjacent to a vehicle repair shop. A secondary arterial

road passes in front of the school and experiences light traffic, with the exception of the hours at the beginning and the ending of the school during school days (typically 7:30–8:30, 13:20–14:00, and 15:30–16:30 LT). The school classrooms follow a rectangular pattern, surrounding the main yard. Thus, each classroom is ventilated from the center of the school and the external outside space. A map of the school and the surrounding area can be found in the [Supporting Information](#).

The selected classroom for the present study was on the first floor on the west wing of the school, with its windows facing the yard to the east side and a flat of apartments with a vehicle repair shop to the west. The size of the classroom was 6.7 × 6.8 × 2.9 m and was occupied by 20 children and their teacher.

The measurements lasted for 3 weeks starting on January 29 (Monday), 2024, until February 16 (Friday), 2024. All of the instruments were measuring continuously during school days and weekends, characterizing both the outdoor and the indoor air.

The collected data were categorized in three time periods:²²

- 8:00 until 13:30 (school hours)
- 13:30 until 16:30 (cleaning period)
- Rest of the day and weekends (nonschool hours)

During the school hours, some classroom windows remained open depending on the weather, while during nonschool hours, they were closed—except for the window used for the sampling lines, which remained always partially open. Between classes, during breaks, the windows facing the yard were opened to ventilate the classroom (the schedule of the school classes is presented in [Table S1](#)).

Instrumentation

A suite of reference monitors and low-cost sensor systems was deployed to measure the air quality inside and outside of the classroom. The FORTH (Foundation for Research and Technology Hellas) mobile laboratory⁴⁶ was used to transport and host a carbon monoxide (CO) (model 300E, API Teledyne), a carbon dioxide (CO₂) (model T360, API Teledyne), nitrogen oxides (NO_x: NO and NO₂) (model T360, API Teledyne), and an ozone (O₃) (model 400E, API Teledyne) monitor. The particle size distribution (size range: 10–710 nm) was measured using a scanning mobility particle sizer (SMPS) (water-based, classifier model 3080, differential mobility analyzer (DMA) model 3081, condensation particle counter model 3787, TSI), with a sheath flow rate of 5 L min^{−1} and a sample flow rate of 1 L min^{−1}.

A Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS 6000 IONICON Analytik GmbH) was used to monitor volatile organic compounds (VOCs) in the classroom. The instrument operated at a sampling flow rate of 0.5 L min^{−1}, with a drift tube voltage of 400 V and a drift pressure of 2.8 mbar. The assignment of these *m/z* values to molecular formulas was performed using ChemCalc⁴⁷ and cross-verified with databases such as the GLOVOCS list.⁴⁸ A maximum tolerance of 10 ppm between theoretical and measured mass and a fixed absolute mass window ($\Delta m < 1.5$ Da) for smaller mass compounds was applied for chemical structure assignments.

At the start of the campaign, the PTR-MS was calibrated in situ using a precision calibration system (liquid calibration unit, LCU; IONICON) to dynamically dilute a standard VOC standard gas mixture (12 compounds; Restek). A multilevel calibration protocol was applied, enabling the determination of compound-specific response factors for the VOCs included in the mixture ([Table S4](#)). These calibrated species were subsequently used to derive the instrument transmission curve, which was then applied to extend the quantitative analysis to the full suite of detected VOCs. Additional information about the PTR-MS data analysis can be found in the [Supporting Information Section S1](#).

A reaction rate constant equal to $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was assumed for all other detected species including also the detected fragments of molecules. For the fragments, it is assumed that the dissociation of the excited protonated intermediates of the parent molecules yields a neutral molecule and the charged fragment detected. Due to the narrow range of reaction rate constants for the protonation of

compounds by the oxonium ion, an uncertainty of less than 30% is expected for the reported concentration values for the majority of the species. The transmission efficiency is mass-to-charge ratio specific and represents what fraction of the ions of certain mass is finally detected. Since the fragments are produced in the drift tube prior to the time-of-flight mass analyzer, the transmission efficiency used corresponds to the mass-to-charge ratio of the fragments (and not the parent molecules), as established by the calibration procedure of the PTR-MS. The compounds for which the concentration was based on the calibration standard are shown in Table S4. The concentrations of the rest of the compounds and fragments in Table S3 are based on the assumed rate constant between the parent compound and the oxonium.

Daily background signal measurements of the PTR-MS were collected via an activated charcoal filter (Supelco Analytics) for 10 min. Additionally, in the context of the PTR-ToF-MS measurements, the total VOC mixing ratio reported in the following sections refers to the sum of all organics detected by the instrument and is listed in Table S3, expressed in units of ppb.

An automated valve switching system was developed to alternate sampling between indoor and outdoor environments. This system utilized two 3-way Swagelok valves, one dedicated to the gas-phase and the other to the particle-phase lines, both controlled via a Pololu Maestro Servo Controller. During school hours (08:00–15:00), the instrument sampled indoors for 80 min and outdoors for 20 min in each cycle. Outside of school hours, the pattern was reversed, with 20 min of indoor and 80 min of outdoor sampling, ensuring representative data collection across the diurnal cycle. The monitors deployed and the PTR-MS remained inside the FORTH mobile laboratory for the duration of the campaign. An 8 m sampling line connected them to the classroom.

Along with the monitors, five ENSENSIA systems^{49,50} were also used for the indoor and outdoor measurements. ENSENSIA is a multiple low-cost sensor system for monitoring outdoor and indoor air quality developed by FORTH. Each system contained low-cost sensors that measured gaseous and particulate species. For CO (B4), NO₂ (B43F), total VOCs (B4), and O₃ (B431), the electrochemical sensors produced by Alphasense Ltd., are used by ENSENSIA. CO₂ is monitored using the COZIR-AH sensor from Gas Sensing Solutions. PM_{2.5} was monitored by two PMS5003 sensors from Plantower.

All gas sensors were initially calibrated by the manufacturer (Alphasense Ltd.) under a laboratory setting using standard reference calibration gases. A calibration certificate is provided for each individual sensor, which establishes its exact sensitivity and electronic baseline zeros for both the working electrode and the auxiliary electrode across standard operational concentration ranges. We converted the raw electronic signals into concentrations using the manufacturer recommended equations and the sensor-specific calibration parameters that Alphasense provides with each sensor (Alphasense Ltd., 2019). The Alphasense VOC-B4 utilizes ethanol as its primary surrogate to establish a linear response from zero to approximately 800 ppb. Before the school campaign, all five ENSENSIA units were colocated outdoors in Patras for 2 weeks, sampling the same ambient air under identical configuration, to verify stability and interunit consistency. During this collocation, we made small adjustments to electronic parameters so that all units agreed, and then we kept those settings fixed during the school campaign. Additional details can be found in the study of Apostolopoulos et al. (2025).⁵¹

Two ENSENSIA systems were located inside the classroom (one near the west window and one further inside the classroom) and three were located outside at the ground level, near the FORTH mobile laboratory. The performance of these systems against reference instruments has been investigated by Apostolopoulos et al. (2025).⁵¹ For example, in the present study, the measurements of the two indoor low-cost CO₂ sensors had a normalized mean error of 9% and 11% against the reference instrument for 8 h school-day averages. At hourly resolution, the errors were at 15% and 17%. Interunit consistency was excellent, with an R^2 of 0.94 and a coefficient of divergence of 0.02 between the two sensors, indicating highly

reproducible readings (Figures S1 and S2). In addition to various other air pollutant sensors, the ENSENSIA devices include a sensor dedicated to measuring total VOCs (TVOCs). The two indoor TVOC sensors exhibited strong interunit agreement, achieving an R^2 of 0.94 between them. Their mean absolute difference was 43.3 ppb, with a mean bias of 3.4 ppb and a relative mean absolute difference of 7%, based on 5 min averages. Figure S4 illustrates their high correlation. Throughout the entire measurement period, Sensor 1 recorded an average TVOC mixing ratio of 620 ± 4.6 ppb, while Sensor 2 measured 615 ± 4.5 ppb. Given their consistent performance and minimal deviation, the average of the two sensors was used for all subsequent analyses. The resulting combined average mixing ratio was 617 ± 4.5 ppb over the monitoring period and 904 ± 16.1 ppb during school hours.

To estimate the emission rates in mg h^{-1} of total VOCs, considering the range of VOCs present inside classrooms,^{7,52} we assumed a VOC average molecular weight of 100 g mol^{-1} . Before the campaign, the five sensor units were colocated and performed ambient measurements outside our laboratory in Patras, Greece, for 2 weeks. Concentrations were derived using the manufacturer's calibration formula, with additional adjustments to the electronic parameters to ensure agreement (interunit consistency) between the two sensor units. These adjustments were used during the school campaign for turning the electronic sensor signal to concentration values following the approach of Apostolopoulos et al. (2025).⁵¹ The monitors were providing measurements every 5 min, while ENSENSIA was reporting values every 2 min.

PTR-MS Measurements

For the quantification of the mixing ratios, a universal reaction rate constant (k) of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was assumed for all detected species. This value was chosen as it represents the median of the typical range for $\text{VOC-H}_3\text{O}^+$ reactions (1.5 to $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). Given that the study aimed to compare the total VOC (TVOC) response of low-cost sensors to the aggregate signal of the PTR-MS, a constant rate was deemed appropriate and is a standard practice in the literature when specific sensitivities for over 100 species cannot be individually calibrated. Data processing was performed using the IONICON Ion-Data Analysis (IDA) software. This allowed for high-resolution peak fitting and the separation of isobaric compounds.

RESULTS AND DISCUSSION

Meteorological Conditions

Significant weather variations were observed during the campaign. The first week, 29/1–4/2 of 2024, was the coldest with significant rainfall observed during the week. The temperature ranged between 4 and 8 °C, with relative humidity exceeding 80% and average wind speed of 30 km h^{-1} . During this first week, the school increased heating, and during breaks, the students remained in the hallways. During the second week, 5–11/2, there was a notable increase in temperature, which ranged from 8 to 20 °C, with sunshine during the day. The relative humidity remained relatively high, at an average level of 70%, but the average wind speed was reduced to 12 km h^{-1} . Finally, the third and final week, 12–16/2, was sunny with temperatures in the 5–15 °C range and an average relative humidity of 70%. There was an increase of the average wind speed compared to the second week (20 km h^{-1}). The weather conditions of the last 2 weeks allowed for full operation of all the available school spaces, including the school yard.

Estimation of the Air-Exchange Rate

To estimate the average air change rate (ACR) during the day, the continuous measurements of indoor and outdoor CO₂ concentrations of the reference monitor were used following the approach of Dovrou et al. (2024).²² The classroom was

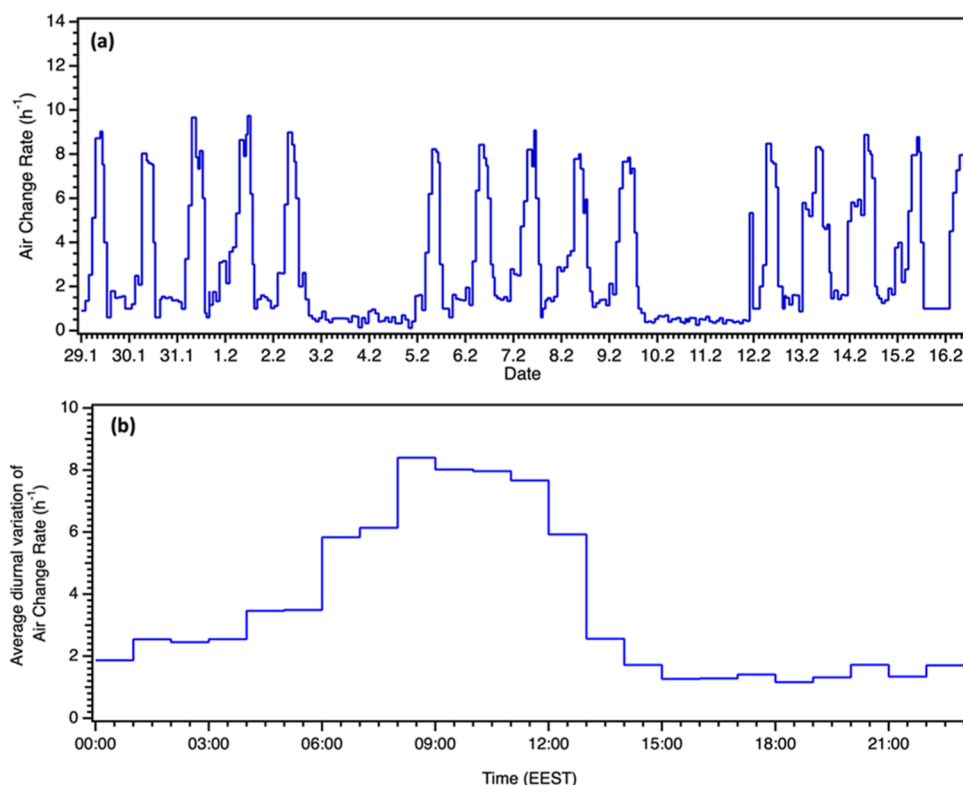


Figure 1. (a) Air change rate (10 min intervals) for the duration of the school measurements and (b) average diurnal variation of the air change rate for the 14 examined school days. The average diurnal variation was estimated by estimating the average ACR per hour for the examined school days. A window remained partially open during the nonschool hours.

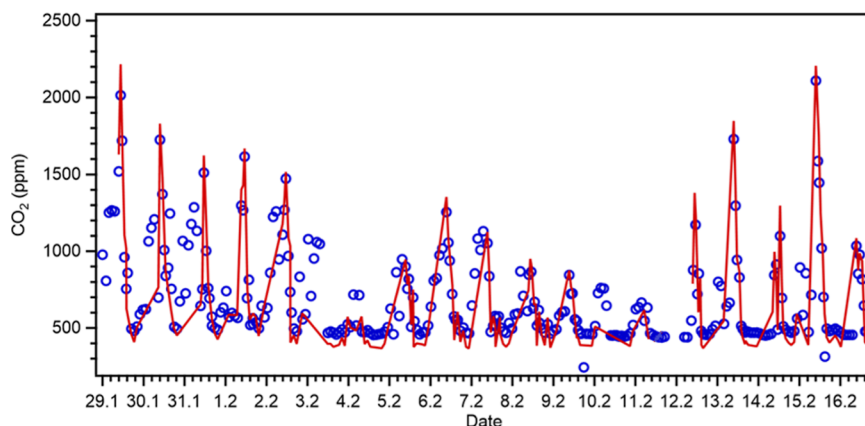


Figure 2. Measured (blue symbols) and box-model predicted (red line) CO₂ in-classroom levels during the campaign using the estimated air exchange rates. The data are presented with 1 h resolution, and the measurements correspond to reference monitor sampling.

assumed to be well mixed. A CO₂ emission rate of 8.8 μg s⁻¹ person⁻¹ was assumed.⁵³ Assuming no other significant indoor sources, the indoor CO₂ concentration, CO_{2in}, is given by

$$V \frac{d\text{CO}_{2\text{in}}}{dt} = \text{VR}(t)(\text{CO}_{2\text{out}}(t) - \text{CO}_{2\text{in}}(t)) + n(t)E_{\text{CO}_2} \quad (1)$$

where V is the volume of the classroom ($V = 132 \text{ m}^3$), t is the time from the beginning of the simulation (s), VR is the ventilation rate ($\text{m}^3 \text{ s}^{-1}$), $\text{CO}_{2\text{out}}$ is the outdoor CO₂ concentration (g m^{-3}), $\text{CO}_{2\text{in}}$ is the indoor CO₂ concentration (g m^{-3}), $n(t)$ is the number of persons in the classroom ($n = 21$ during classes and $n = 0$ during the rest of the time), and E_{CO_2} is the average CO₂ emission rate ($\text{g s}^{-1} \text{ person}^{-1}$). This

simple box model uses as inputs the volume of the classroom, which remained unchanged, the number of people within the classroom, which changed depending on the class and time of the day, the average CO₂ emission rate per person, and the indoor and outdoor CO₂ levels as a function of time. Equation 1 was solved at 10 min intervals, assuming that the ventilation rate remained constant during each interval. For each time interval, the air change rate ($\text{ACR} = \text{VR}/V$) was estimated by minimizing the difference between the calculated and the observed indoor CO₂ concentrations, using the measured $\text{CO}_{2\text{out}}(t)$ as an input to the model.

The estimated average ACR during classes was 6.4 h⁻¹ (Figure 1), within the range of previously reported values of ACR in a Greek primary school classroom during the winter.²²

Assuming a 20% reduction in the number of students in the classroom, the ACR increased by 18.6%, indicating the magnitude of the sensitivity of this parameter to the occupancy of the classroom. The ACR during the operation of the classroom was mostly above the minimum recommended standards, 15 ft³ min⁻¹ person⁻¹ (around 4 h⁻¹ for this classroom), by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE).⁵⁴

During the weekend, when classrooms were unoccupied and windows remained closed, indoor CO₂ concentrations decayed toward outdoor levels, indicating low ventilation (<1.0 h⁻¹). On the basis of CO₂ decay analysis using eq 1 and assuming zero emissions of CO₂ in the room, the average ACR was 0.6 h⁻¹. Please note that during most of the study, the outdoor and indoor concentrations of CO₂ were not equal to each other; therefore, there was a driving force for the change of the indoor CO₂ levels even when the classroom was empty. This difference was partially due to the temporal variability of the CO₂ levels outside the classroom. The second reason was that during these periods with no occupants in the classroom, the windows were generally closed and therefore the air exchange was low. This resulted in a slow approach of the indoor CO₂ levels toward the outdoor ones and prevented the system from reaching a steady state. This behavior can be seen during the two weekends. In the few hours where the indoor and outdoor concentrations were practically the same, a default exchange rate value was assumed. This did not affect the results of the study not only because it was a rare event but also because the VOC emissions were zero during these periods, and the ozone removal rates were also low.

The mean absolute error and bias between the predicted and measured CO₂ concentrations (Figure 2) were 10.3 ppm and -6.2 ppm, while the normalized mean error (NME) was approximately 3% (Table 1). Figure 2 should not be viewed as

Table 1. Mean Absolute Error, Mean Bias, and Normalized Mean Error^a of Monitor Pollutant Measurements vs Model Estimations and ENSENSIA Measurements vs Model Estimations

	mean absolute error	mean bias	normalized mean error (%)
CO _(monitor) (ppb)	0.08	0.06	13.6
CO _(ENSENSIA) (ppb)	0.5	-0.2	74.3
CO _{2(monitor)} (ppm)	10.3	-6.2	2.8
CO _{2(ENSENSIA)} (ppm)	33.0	20.6	6.1
NO _{2(monitor)} (ppb)	5.6	1.3	31.1
NO _{2(ENSENSIA)} (ppb)	8.0	0.5	55.1
PM _{1(monitor)} (μg m ⁻³)	0.4	-0.2	7.6
PM _{2.5(ENSENSIA)} (μg m ⁻³)	4.2	-0.5	41.6

^aThe model performance metrics are defined in the Supporting Information Section S2.

an independent validation of the model, but rather it illustrates the consistency of the time-resolved ACR estimation with the measured CO₂. The estimated ACR was then used for the other examined species and for the sensor measurements presented herein.

Analysis of CO, NO₂, and Fine PM Levels in the Classroom

The estimated ACR values were used as an input to test the hypothesis that indoor CO, NO₂, and PM₁ and PM_{2.5} levels were due practically exclusively to outdoor sources. The ACR

values were calculated based on the CO₂ measurements, and the indoor pollutant levels were then estimated based on the ACR and their measured outdoor concentrations (eq 2). Assuming no sources or sinks in the classroom their concentrations (C_{in}) are described by

$$V \frac{dC_{in}}{dt} = VR(t)(C_{out}(t) - C_{in}(t)) \quad (2)$$

where C_{out} is the corresponding outdoor pollutant concentration.

Figure 3 shows the model estimated and measured concentrations inside the classroom by the reference monitors for the duration of the campaign. The mean absolute error and mean bias of measured vs modeled estimated CO were equal to 0.08 and 0.06 ppb respectively, and the NME was 13.6% (Table 1). The corresponding NMEs of monitor measurements versus model predictions of NO₂ and PM₁ were below 30%, indicating relatively accurate representation of the measured pollutant levels by the model (Table 1). This good agreement suggests that our hypothesis of negligible indoor sources is supported by measurements.

Equation 2 does not include indoor deposition or chemical loss processes assuming that the rates of these processes were low compared to the exchange with the environment. The settling velocity of particles smaller than 1 μm is less than 0.1 m h⁻¹ under low indoor turbulence conditions,⁵⁵ supporting our assumption. The small and nonsystematic deviations between modeled and measured concentrations suggest that this assumption introduced small errors in the model predictions for NO₂ and CO. For NO₂, in some periods, the model underpredicts its indoor levels by a few ppb and in some other it overpredicts. However, the model is not systematically biased toward overprediction. These differences may reflect spatial differences between the outdoor monitoring location and the air entering the building but also uncertainties of the NO₂ low-cost sensor measurements which are higher than those of PM₁. The lack of a systematic overprediction of the model neglecting NO₂ losses on surfaces is also consistent with our hypothesis that this was not a dominant sink in this environment.

The measured indoor CO₂ concentrations were up to 2000 ppm, substantially higher than the measured outdoor levels (~500 ppm). Similar indoor CO₂ ranges have been reported in naturally and mechanically ventilated school environments across Europe.^{22,56,57} In contrast, indoor NO₂ concentrations were comparable to outdoor levels, indicating a dominant influence of outdoor urban air pollution. These NO₂ levels are within the range of previously reported urban environments.^{22,58,59} The average PM concentration measured during the class periods in the classroom was 10–20 μg m⁻³, which is comparable to values reported in schools located in urban areas.^{17,58}

Measurement of VOCs

The total VOC levels were measured using the corresponding ENSENSIA sensor (Figure S3). The total VOC mixing ratios represent the mean value of the two indoor sensors placed in the classroom. The two indoor total VOC (TVOC) sensors exhibited strong interunit agreement (Figure S4), with an R² of 0.94 between them. Their mean absolute difference was 43.3 ppb, with a mean bias of 3.4 ppb and a relative mean absolute difference of 7%, based on 5 min averages. Throughout the entire measurement period, Sensor 1 recorded an average

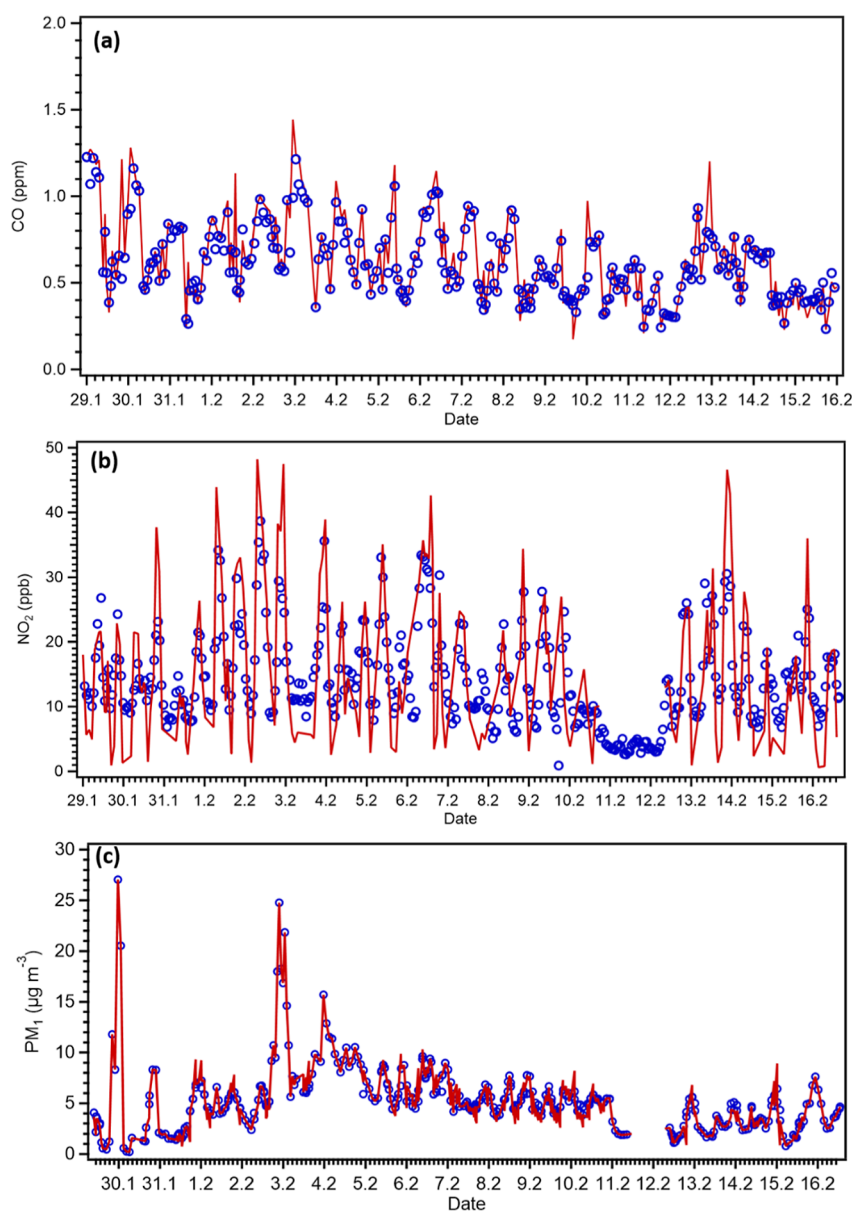


Figure 3. Measured (blue symbols) and predicted (red line) (a) CO, (b) NO₂, and (c) PM₁ in-classroom levels. The predicted levels are obtained from the box model of the classroom using the estimated air exchange rate and the measured ambient concentrations. The data are presented with 1 h resolution, and the measurements correspond to monitor sampling. Due to lack of outdoor measurements, model simulations were not conducted for 12/2.

TVOC mixing ratio of 620 ± 4.6 ppb, while Sensor 2 measured 615 ± 4.5 ppb. Given their consistent performance and minimal deviation, the average of the mixing ratio was 617 ± 4.5 ppb over the monitoring period and 904 ± 16.1 ppb during school hours. The average discrepancy among the three outdoor sensors was approximately 10%.

The indoor sensor measurements were elevated compared with the outdoor levels during classes and specifically during arts and crafts classes. The average indoor level during classes was 904 ppb, while the outdoor mixing ratio was 516 ppb. The 80% difference indicates major indoor VOC sources. The extremely high values (more than 1000 ppb) reported for short periods were either during periods when local outdoor sources affected air quality in the classroom or during cleaning periods. Typically, VOC levels inside classrooms range from a few parts per billion up to more than 1000 ppb, depending on the

occupancy, ventilation, cleaning materials, and building materials.^{22,34} The observed VOC levels in this classroom were high but generally consistent with those previously reported in similar indoor environments.

During school hours, the average total VOC mixing ratio measured in the classroom by the PTR-MS was 465 ± 20.8 ppb. The PTR-ToF-MS detected 165 *m/z* signals during the campaign. Among the individual VOCs detected from the PTR-ToF-MS during school hours, the average mixing ratio of the most important ones was: acetaldehyde 54.1 ppb (Indoor/Outdoor (I/O): 8.2), methanol 20.6 ppb (I/O: 5.6), acetone 19.5 ppb (I/O: 5.2), ethanol 13.7 ppb (I/O: 9.4), formaldehyde 11.7 ppb (I/O: 6.4), styrene 0.3 ppb (I/O: 1.8), C₈ aromatics 2.1 ppb (I/O: 1.1), C₉ aromatics 1.7 ppb (I/O: 1.6). The levels of these compounds were a factor 1.1–9.4 lower outside the school during the class periods, indicating that

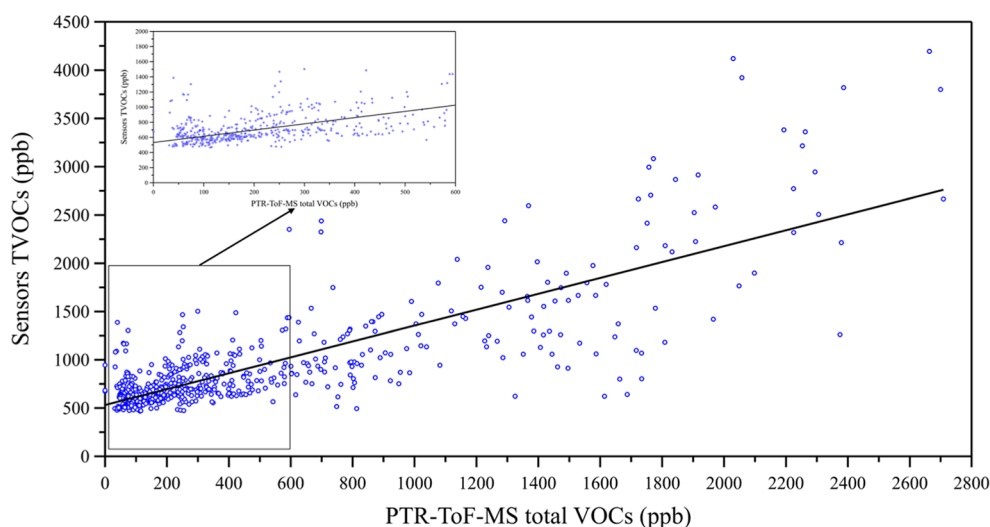


Figure 4. Correlation graph of the average TVOC measured by the ENSENSIA sensors versus the PTR-ToF-MS total VOCs, based on 5 min averages. The black line represents the corresponding least-squares fit line: $y = 0.823x + 531.9$. The inset shows only the values below 600 ppb.

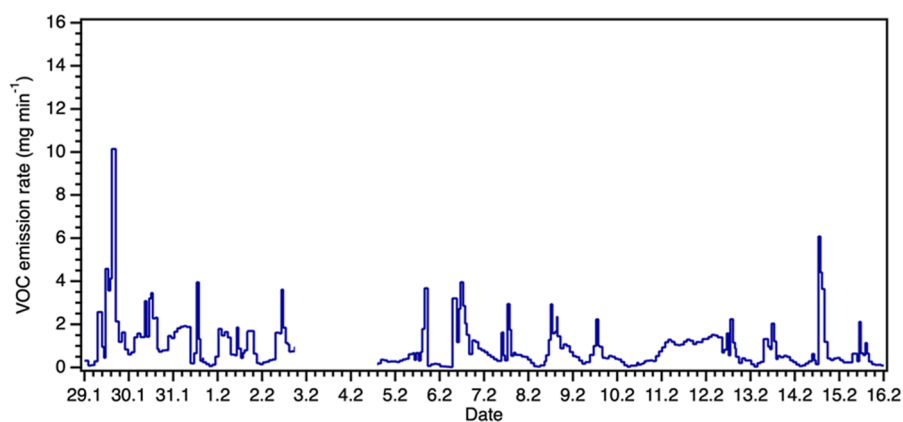


Figure 5. Effective VOC emission rate (10 min intervals) for the duration of the campaign, as estimated by the model based on the ENSENSIA measurements.

there were strong sources inside. The PTR-ToF-MS also detected the fragments C_3H_2 , C_3H_4 , and C_3H_6 , with average indoor mixing ratios of 71.4 ppb (I/O: 11.7), 107.5 ppb (I/O: 10.0), and 83.8 ppb (I/O: 12.7), respectively. These fragments have been previously identified in the literature: C_3H_2 is a possible fragment of compounds such as isoprene or pentanal; C_3H_4 originates from over 20 VOCs including alcohols, aldehydes, esters, and acetone; and C_3H_6 is typically associated with alcohol and ester fragmentation.^{48,60,61} Collectively, the above-mentioned VOCs and fragments accounted for approximately 80% of the average total VOC mixing ratios indoors as measured by the PTR-MS during school hours. The list of VOCs considered for the TVOC calculation is presented in Table S3. The fragment ions were included in the present analysis because their mixing ratios within the classroom environment were substantial and the low-cost VOC sensor used in this study appears to be sensitive to at least some of their parent molecules. Excluding fragment ions at this stage could result in an underestimation of the overall VOC load to which the sensors are effectively responding in this classroom environment. Even if these fragments are included in the summation (as ppb or similar unit that expresses number of molecules), the sum is underestimating the total VOC concentration because of undetected compounds (e.g., small

alkanes) by the PTR-MS. However, it is a much better estimate of the total VOC levels (in ppb) compared to the sum neglecting them. Please note that these fragments do not represent the whole molecule (the remaining piece or pieces are usually not charged and therefore are not detected), so the sum of the mass concentrations or carbon concentrations is also affected by the undetected piece or pieces of the fragmented molecule.

The major detected VOCs in this study have also been reported in previous studies investigating classroom air quality.^{4,22,57,62,63} In these studies, the reported mean of the TVOC mixing ratio ranged from close to zero to 600 ppb with averages between 10 and 40 ppb.^{4,22,57,62,63} For the conversion from $\mu g m^{-3}$ to ppb, a temperature of 20 °C and an average molar mass of 100 g mol⁻¹ were assumed. In the present study, TVOC concentrations averaged 465 ppb indoors during school hours and 170 ppb during nonschool hours, values substantially higher than the mean concentrations reported in previous studies. However, most of the aforementioned studies employed offline measurement techniques and their samples included periods in which the classroom was not occupied. In our previous study,²² we studied a Greek elementary school classroom located in the outer suburbs of a city with low pollution levels, with its windows open most of

the time. Both of these factors led to significantly lower VOC levels in the classroom. In contrast, the classroom investigated in the present study appears to be influenced by both substantial indoor emission sources and elevated outdoor pollution levels, leading to significant accumulation of VOCs indoors. Additional analysis of the extended PTR-MS results and the corresponding source apportionment will be the focus of future work and is beyond the scope of the present study.

The total VOCs measured by the PTR-ToF-MS had an R^2 of 0.67 with the combined low-cost sensor total VOC measurements (Figure 4). While the sensors were responsive to VOC changes detected by the PTR-ToF-MS, they consistently overestimated the total VOC mixing ratio, particularly at lower mixing ratios, particularly below about five hundred parts per billion. Further correlation analysis between individual PTR-ToF-MS species and sensor total VOC readings revealed that 26 compounds exhibited R^2 values above 0.2, with 17 of these exceeding 0.4 (Table S2). Overall, the performance of this VOC sensor in this specific environment is encouraging.

Emission Rates of Total VOCs

The VOC emission rates (ERs) were estimated for the time periods of classes, breaks, afternoon, and nonschool hours. The VOC ER was calculated for 10 min time intervals, using the following equation.

$$ER(t) = V \frac{\Delta VOC_{in}}{\Delta t} - VR(t)(VOC_{out}(t) - VOC_{in}(t)) \quad (3)$$

where ER is the total VOC emission rate (mg min^{-1}). The $\Delta VOC_{in}/\Delta t$ term was estimated for 20 min intervals and was assumed to be constant during these periods.

Figure 5 presents the effective VOC ERs for the duration of the campaign. The average rate for classes was 1.1 mg min^{-1} (range of $0.1\text{--}4.6 \text{ mg min}^{-1}$). One should note that these values correspond to the total VOCs, as measured by the specific low-cost sensor. Considering, for example, the link between the sum of the VOCs measured by the PTR-MS and the mixing ratios of the total VOCs reported by the low-cost sensors, the equivalent emissions for the PTR-MS VOCs would be 20% higher or 1.3 mg min^{-1} on average.

High VOC emission rates (10.2 mg min^{-1}) were estimated at 14:45 on January 29. A deep cleaning of the classroom using higher quantities of cleaning products was conducted on that day. A high rate of 6 mg min^{-1} was also estimated on February 14 at 12:30. This elevated emission rate was attributed to the use of craft and painting materials in the class of environmental studies. Figure 6 depicts the estimated total VOC emission rate during each class. Elevated emissions were observed during the art class, environmental studies, and informatics. The maximum ER of 4.6 mg min^{-1} was estimated for the environmental studies. High emission rates were also estimated for cleaning periods.

Figure 7 presents the comparison of the ENSENSIA total VOC measurements, and the box model presents predictions for the ENSENSIA indoor VOC estimates, for the duration of the campaign.

$$V \frac{dVOC_{in}}{dt} = ER(t) + VR(t)(VOC_{out}(t) - VOC_{in}(t)) \quad (4)$$

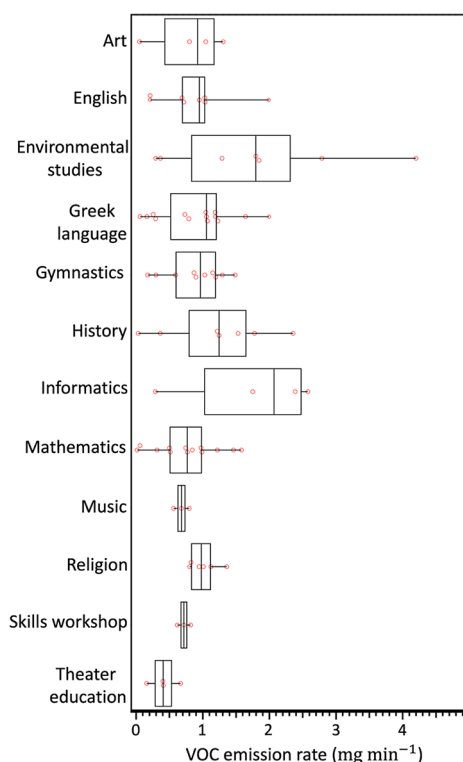


Figure 6. VOC estimated emission rate for each class, as estimated by the model for the ENSENSIA measurements.

The results reveal an efficient representation of the indoor VOC levels by the model. The mean error between measurements and model estimation was 7.5 ppb. The mean bias and NME were 2.4 ppb and 12%, respectively. Once more, this comparison should be viewed as a consistency check for the estimated emission rates.

Irga et al. (2024) reported emission rates of four VOCs (acetone, monoterpenes, acetic acid, and isoprene), with an average total value of 0.3 mg min^{-1} .²¹ In comparison, the ER reported herein (average 1.1 mg min^{-1} , range of $0.1\text{--}4.6 \text{ mg min}^{-1}$) is approximately five times higher, with the elevated values corresponding to activities associated with high VOC emissions. It should be emphasized that the ER estimated in this work corresponds to the total VOCs measured by the ENSENSIA, whereas the average total value calculated from the study of Irga et al. (2024) was based on only four VOCs.²¹

Ozone Sinks

Ozone is a highly reactive species participating in various gaseous and surface reactions. Inside a classroom, O_3 can also be removed via reactions on surfaces and by its reaction with NO .^{64,65} The variation of the ozone levels indoors assuming an effective removal rate constant (k_{O_3}) can be described by

$$V \frac{dO_{3in}}{dt} = VR(O_{3out}(t) - O_{3in}(t)) - k_{O_3}(t)O_{3in}(t) \quad (5)$$

We have used this equation together with indoor and outdoor ozone concentration measurements by the reference monitor to estimate the removal rate constant. During school hours, the average estimated k_{O_3} was 10 h^{-1} . The model was able to reproduce the O_3 measurements during periods when the classroom was empty neglecting O_3 losses to surfaces. Different k_{O_3} were examined, determining k_{O_3} up to 1.2 h^{-1}

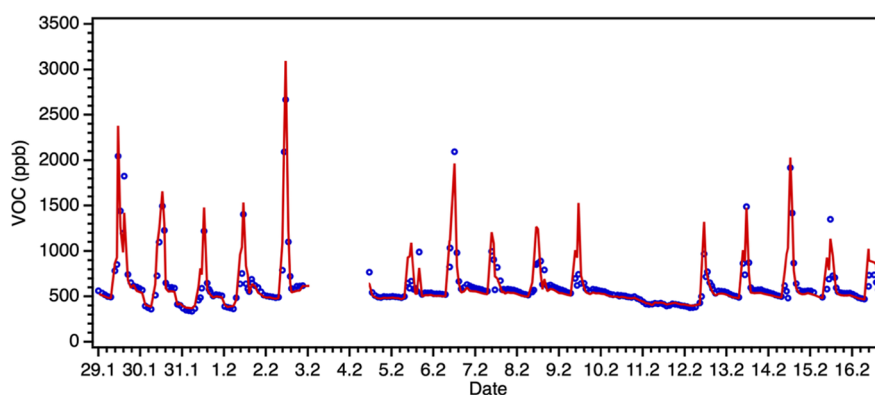


Figure 7. Measured (blue symbols) and predicted (red line) total VOC in-classroom levels. The predicted levels are obtained from the box model of the classroom using the estimated air-exchange rate and the measured ambient concentrations. The data are presented with 1 h resolution, and the measurements are from the ENSENSIA sensor.

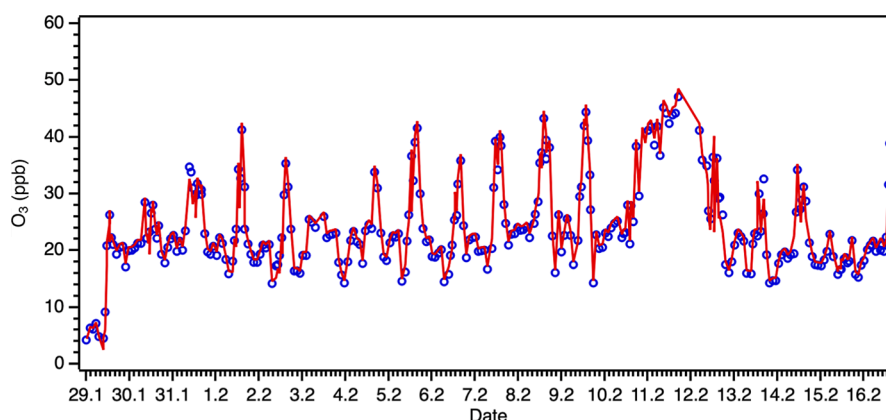


Figure 8. Measured (blue symbols) and predicted (red line) O₃ in-classroom levels. The predicted levels are obtained from the box model of the classroom using the estimated air-exchange rate, the measured ambient concentrations, and the estimated indoor loss rates. The data are presented with 1 h resolution, and the measurements correspond to monitor sampling.

provides acceptable agreement with the observations during these periods of inactivity. The low k_{O_3} ($0\text{--}1.2\text{ h}^{-1}$) estimated values when the classroom was empty are consistent with the absence of carpets or other fabrics in the room. During nonschool hours, the measurements could be reproduced assuming that $k_{O_3} = 0$. During the cleaning period, the calculated k_{O_3} was 0.2 h^{-1} . Using these three rate constants for the cases of nonschool hours, classes and cleaning period which were all precisely known, the model's indoor O₃ estimations had a good agreement with measured concentrations (Figure 8). This agreement was mainly due to the fact that the predicted O₃ concentrations were determined by the outdoor levels and the ACR. The mean absolute error was 4 ppb, the mean bias was -1.5 ppb , and the NME was 30%.

The relatively elevated indoor O₃ concentrations ($>20\text{ ppb}$) observed mainly during school hours are primarily explained by the combination of high outdoor O₃ levels and efficient natural ventilation of the classroom. Indoor concentrations were moderated by loss processes, with an average estimated O₃ rate of 10 h^{-1} .

CONCLUSIONS

During classes, the average air exchange was 6.4 h^{-1} . The presence of windows on both the east and west sides of the classroom facilitated efficient ventilation, reaching an air change rate of 9.7 h^{-1} , when all windows were opened during

school operation. The concentrations of CO, NO₂, and O₃ were within the acceptable limits according to the WHO guidelines. The levels of PM₁ were low, not exceeding $10\text{ }\mu\text{g m}^{-3}$ during school hours.

Elevated VOC levels were observed during school hours, particularly during art class, environmental studies, and theater education, as well as during cleaning periods. In-classroom sources, and specifically arts and crafts materials and cleaning products, were identified as major contributors. An average effective VOC emission rate of 1.3 mg min^{-1} (based on the PTR-MS measurements) was calculated for classroom activities. Emitted VOCs included formaldehyde, acetaldehyde, acetone, methanol, ethanol, C8–C9 aromatics, etc. The corresponding effective emission rate based on the measurements of the ENSENSIA low-cost total VOC sensor was 1.1 mg min^{-1} . This effective VOC emission rate depends on the type and performance of the deployed low cost sensors. A significantly higher average effective rate of 13.4 mg min^{-1} was estimated during the cleaning period, highlighting cleaning products as a dominant VOC indoor source. It is noted that the observation of elevated VOC emissions in certain classes relative to others warrants further investigation, particularly with respect to the source apportionment of individual VOC species contributing to these differences. Such analyses are planned to be part of future research.

In this specific classroom, relying only on natural ventilation, there were periods, especially in the colder days when the

windows were occasionally closed, that the ventilation was slow enough to allow the buildup of CO₂. At the same time, there were occasionally high VOC emission levels in specific classes (due to the use of markers, glue, etc.) that also led to high VOC levels. These results can be viewed as an example of how bad things can get in a specific classroom if several factors contribute at the same time (low ventilation plus activities leading to high VOC emissions). Based on the O₃ indoor and outdoor measurements and the estimated air change rate, the calculated O₃ loss rate constant during classes was 10 h^{−1}.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestair.6c00224>.

Supporting Information includes Section S1 presenting additional experimental information, Section S2 providing the metrics definitions, Figure S1 showing the hourly CO₂ levels by ENSENSIA, Figure S2 showing the hourly averaged CO₂ levels by ENSENSIA, Figure S3 presenting the indoor VOC timeseries measured by PTR-MS, Figure S4 presenting the correlation of the two VOC indoor ENSENSIA sensors, Figure S5 showing the location of the school and the areas of interest, Figure S6 presenting the indoor average particle number size distribution, Figure S7 showing the hourly number concentration timeseries throughout the campaign, Table S1 showing the classroom schedule, Table S2 presenting the R² between individual VOCs measured by PTR-MS, and Table S3 presenting the list of PTR-MS-detected VOC species (PDF)

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Notes

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