Supplementary Material

Can carbon dioxide be a good indicator for formaldehyde in residences?—Monte Carlo modelling for a whole year

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This supplementary material (18 pages) includes 8 sections, 13 figures and 1 table.

S1. Indoor temperature of naturally ventilated residences

The indoor temperature of 9 naturally ventilated residences in Beijing was measured from Nov. 14, 2016 to Nov. 13, 2017, and the hourly mean and standard deviation (SD) are presented in Figure S1. The indoor temperature varied between 16.6 °C and 32.5 °C. This measured range was used as the indoor temperature input for the Monte Carlo (MC) simulation for the naturally ventilated scenario.

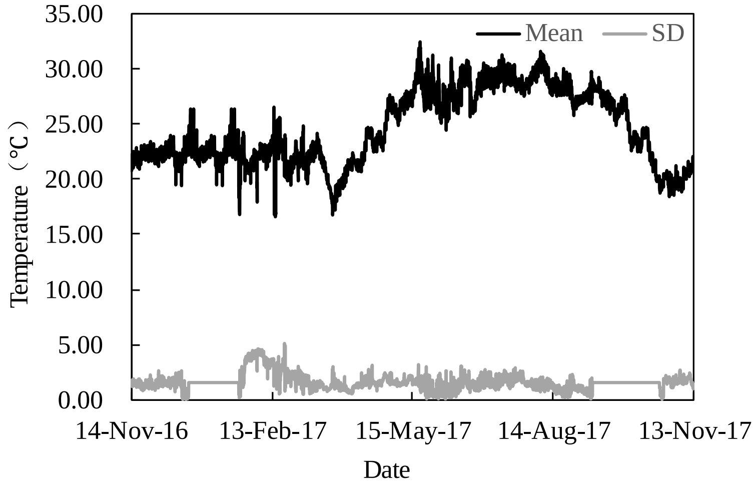
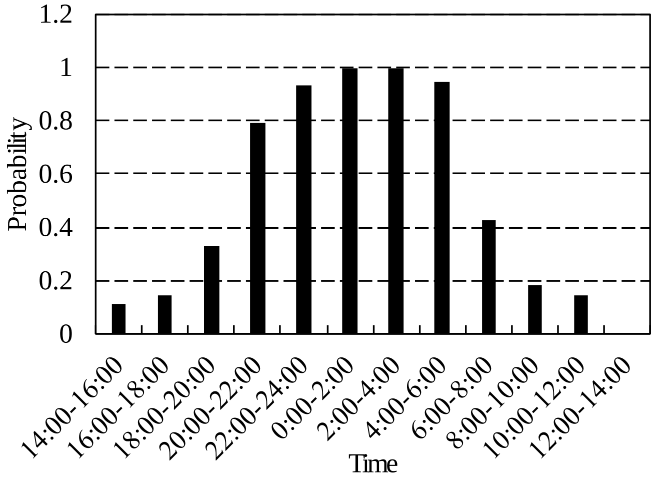


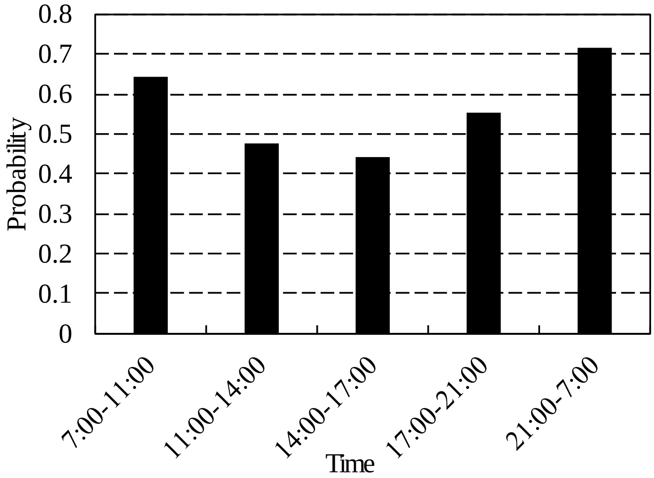
Figure S1. Variation in indoor temperature of naturally ventilated residences in Beijing.

S2. Room occupancy in Beijing residences

The room occupancy in Beijing residences was determined based on an online investigation conducted by Cheng (2018), in which a questionnaire was answered by 1058 subjects from different families. The probability of room occupancy was calculated based on the questionnaires, and the results illustrated in Figure S2 were used as inputs to calculate hourly CO_2 emission rates.



(a)



(b)

Figure S2. Probability of room occupancy in Beijing residences and (a) weekdays and (b) weekends.

S3. Outdoor monthly CO_2 concentration

The monthly average outdoor CO_2 concentrations measured by the Shangdianzi (40°39′ N, 117°07′ E) global atmospheric watch station in Beijing during 2007–2013 are presented in Figure S3 (Xia 2016).

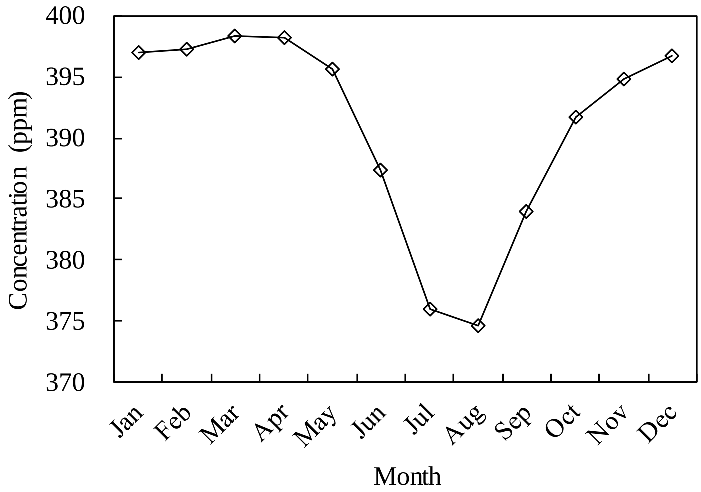


Figure S3. Monthly average outdoor CO_2 concentrations at Shangdianzi station (Xia 2016).

S4. Determination of emission parameters for composite building materials

The foaming agent and joint materials used in the door and furniture installations were treated as composite building materials in this study. A first-order exponential empirical model was used to describe the long-term emission characteristics of the composite building materials, because there was not enough data in the emission database to determine the emission parameter distributions of these materials. We derived the parameters based on the relationships between building material emission characteristics and indoor formaldehyde concentrations. We reviewed long-term indoor formaldehyde measurement results in China from literature, collecting 22 studies with 30 series of long-term formaldehyde concentration data. Regressing the variations in indoor formaldehyde concentration yielded a total of 30 decay constants. The decay constants followed a lognormal distribution with μ = -9.03 and σ = 0.89. The derivation process and results are presented in detail in our recently accepted paper (Liang 2019).

The emission rate constants were derived based on a technical standard in China (JGJ/T 436-2018). The standard gives four different emission levels (F1–F4) and their emission rate limits of 0.01 mg/(m^2·h), 0.03 mg/(m^2·h), 0.06 mg/(m^2·h), and 0.12 mg/(m^2·h), respectively. By assuming that the four different emission levels corresponded to P05, P50, P75, and P95 of the emission rate distribution, a lognormal distribution fitted the initial emission rate constant well with μ = -3.6 and σ = 0.98.

S5. MC framework validation

To validate the credibility of the MC framework used in this study, formaldehyde concentrations were measured in 22 residences from 2016 to 2017, and four different seasons were included for each residence.

Formaldehyde concentration was measured using the 3-methyl-2-benzothiazolinone hydrazone (MBTH) spectrophotometric method in window-closed conditions. To analyze the formaldehyde concentrations by the active sampling method, 0.4 mL of 10 g/L ferric ammonium sulfate solution was added to the sampling tube. The tube was shaken and then held for 15 min, during which formaldehyde was converted into a blue cationic dye by the MBTH. The light absorbance was measured using a spectrophotometer at 630 nm (Unic 7200, China). Quantification of formaldehyde by spectrophotometric method was assured with standard calibration. An aqueous 1.00 μg/mL formaldehyde solution was used as a standard solution for calibration. The calibration solutions were prepared by injecting specific amounts of the standard solution into glass tubes containing MBTH to a total volume of 5 mL. Different formaldehyde concentrations in the calibration solutions were obtained by adjusting the volume of formaldehyde aqueous solution and MBTH. The calibration solutions were subjected to the same analytical procedures as the test samples. By measuring the light absorbance of the yielded blue solution, a calibration curve for light absorbance versus formaldehyde content was obtained. A total of ten points with R^2>0.99 were used. Thus, the formaldehyde concentration of the sampled air could be calculated using the calibration curve. The detection limit of this method was 0.056 μg and the recovery of formaldehyde was 90–105%. Instrument error from the spectrophotometer and sampling procedure was controlled by routine operational maintenance and standard sample calibration.

According to the date of decoration completion and measurement conducted, the time interval between them could be calculated. A comparison between the measured and predicted formaldehyde concentrations is presented in Figure S4, showing that the measured values were within the ranges of the simulation results.

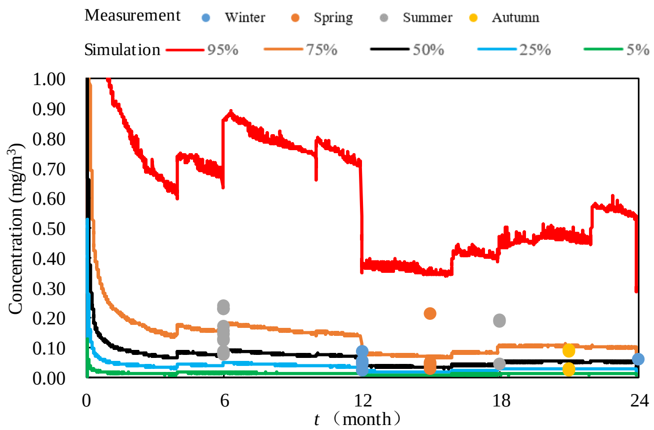


Figure S4. Comparison of measured and MC simulated formaldehyde concentrations.

S6. Long-term CO_2 and formaldehyde concentrations

The mean concentrations of indoor formaldehyde and CO_2 in the mechanical ventilation scenario are presented in Figure S5. Due to the constant ventilation rate, the variations in concentration remained consistent with emission rate. A weekly cyclic change was observed for CO_2 in all seasons, whereas the emission rate and concentration of formaldehyde decayed continuously. This decay was very slow, except for the first few months after completion of the building construction.

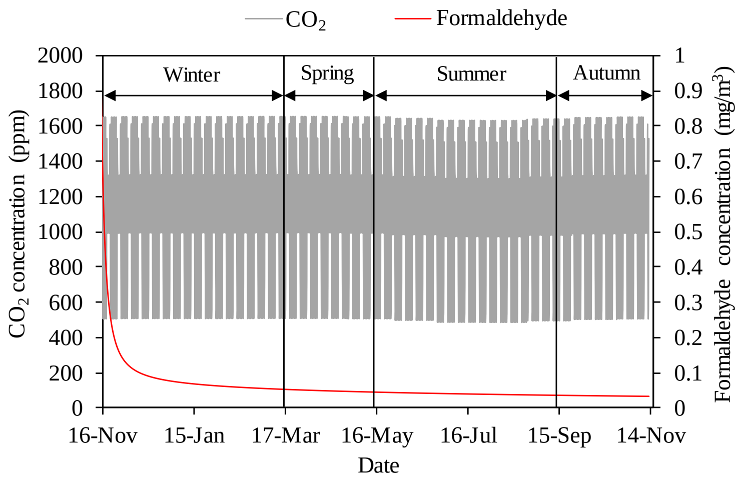


Figure S5. Mean indoor formaldehyde and CO_2 concentrations in the mechanical ventilation scenario.

The mean indoor concentrations of formaldehyde and CO_2 in the natural ventilation scenario are presented in Figure S6, illustrating their differences in variations over the year. CO_2 concentration was highly related to room occupancy and window-opening behaviors, and since these inputs remained the same for weekdays and weekends in each season, the CO_2 concentration varied cyclically. The average CO_2 concentration in the summer was the lowest because of the longest window-opening duration in this season, whereas no large differences occurred in other seasons. Formaldehyde concentration increased and decayed daily with window opening behavior. The overall trend was decreasing during the first few months and then remained relatively constant.

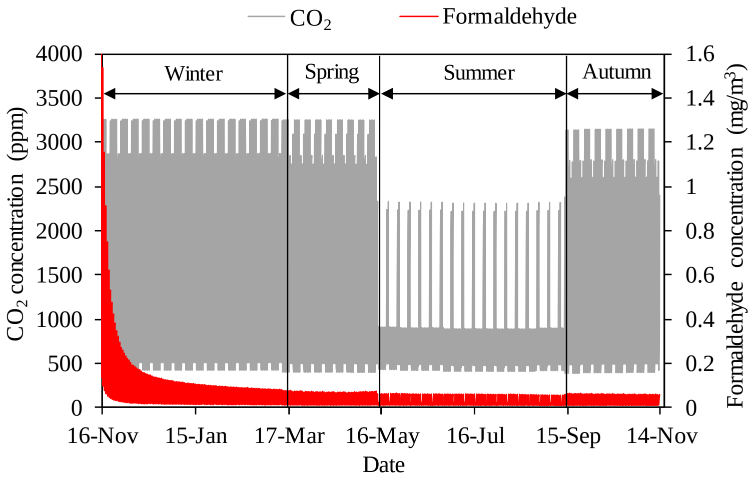


Figure S6. Mean indoor formaldehyde and CO_2 concentrations in the natural ventilation scenario.

S7. Short-term concentrations and correlations

Variable CO_2 emission rate

The mean emission rates and concentrations of CO_2 and formaldehyde on weekdays for the natural ventilation scenario in the summer, autumn, and winter are presented in Figures S7–S9.

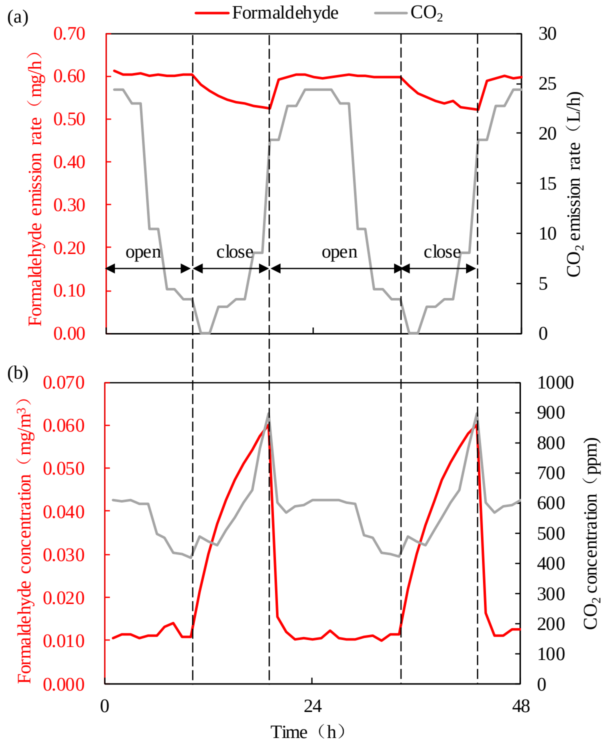


Figure S7. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on weekdays in the summer (Jun. 22–23). The two-way arrows below “open” and “close” represent periods of window-open and window-closed states.

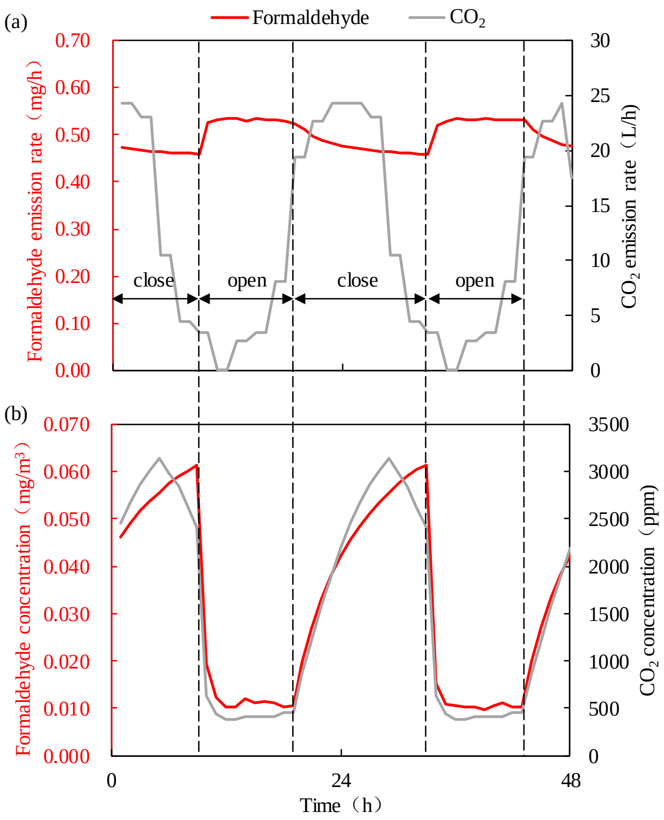


Figure S8. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on weekdays in the autumn (Sep. 21–22).

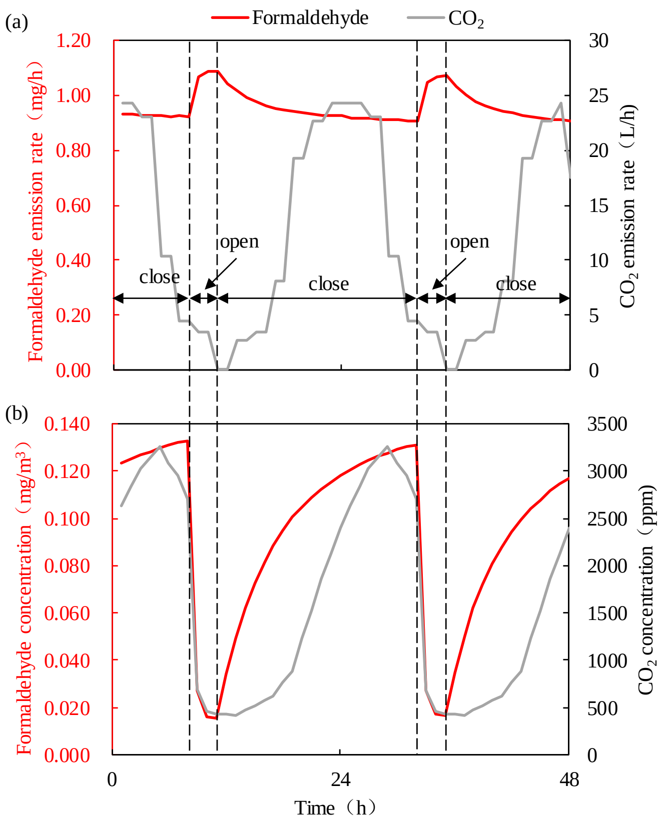


Figure S9. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on weekdays in the winter (Dec. 22–23).

Constant CO_2 emission rate

The mean emission rates and concentrations of CO_2 and formaldehyde on the weekends for the natural ventilation scenario in the summer, autumn, and winter are presented in Figures S10–S12.

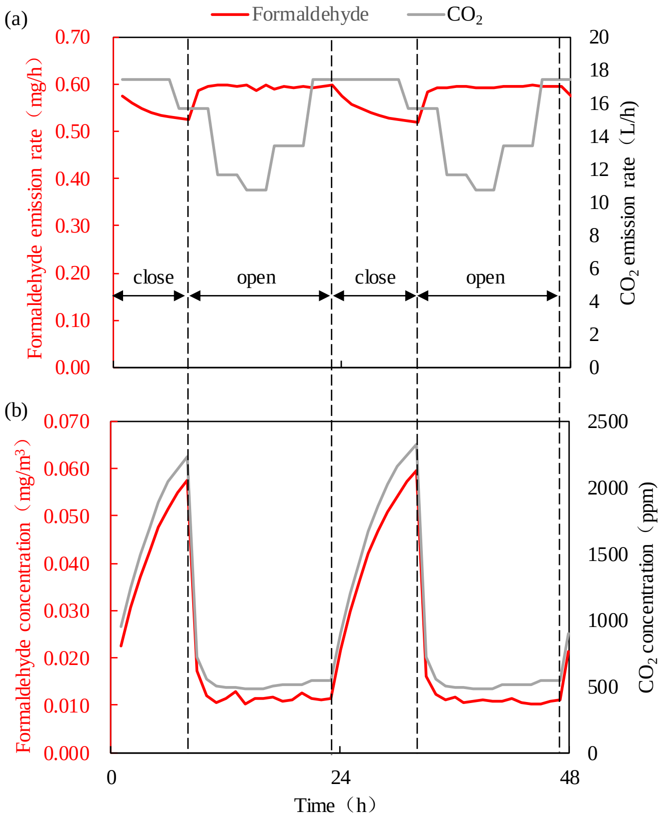


Figure S10. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on a summer weekend (Jun. 24–25).

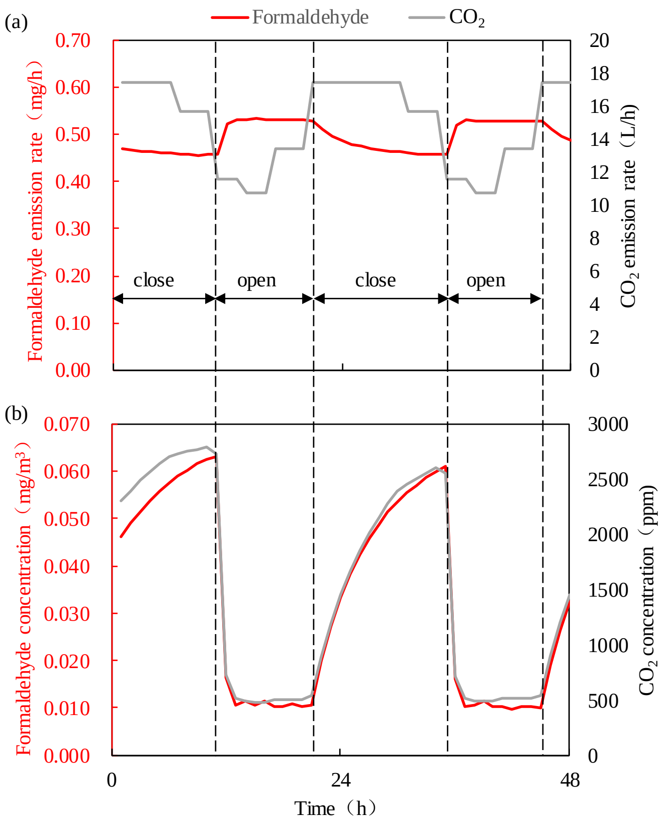


Figure S11. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on an autumn weekend (Sep. 23–24).

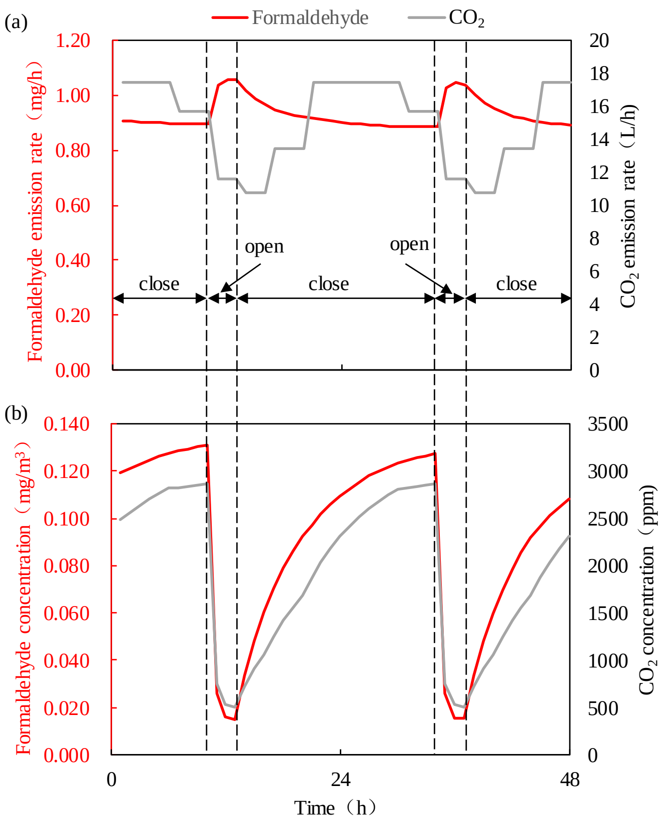


Figure S12. Mean formaldehyde and CO_2 (a) emission rates and (b) concentrations in the natural ventilation scenario on a winter weekend (Dec. 24–25).

S8. Correlation validation of natural ventilation scenario

To validate the correlation between CO_2 and formaldehyde in the natural ventilation scenario, a field experiment was conducted in a dormitory at Tianjin University on Oct. 17–18, 2018. The source information, window-opening state, and Pearson correlation coefficients are given in Table S1. Four students were in the room when the dormitory was occupied. Figure S13 presents the indoor CO_2 and formaldehyde concentrations in the dormitory at different window-opening states.

Table S1. Room occupancy and window-opening state of the dormitory in different stages.

Stage No.	Room occupied?	Window state	Pearson correlation coefficient
Stage 1	Y	Close	0.84
Stage 2	Y	Open	0.76
Stage 3	N	Close	0.34
Stage 4	N	Open	0.77

Note: “Y” and “N” indicate that the room was occupied and not occupied, respectively.

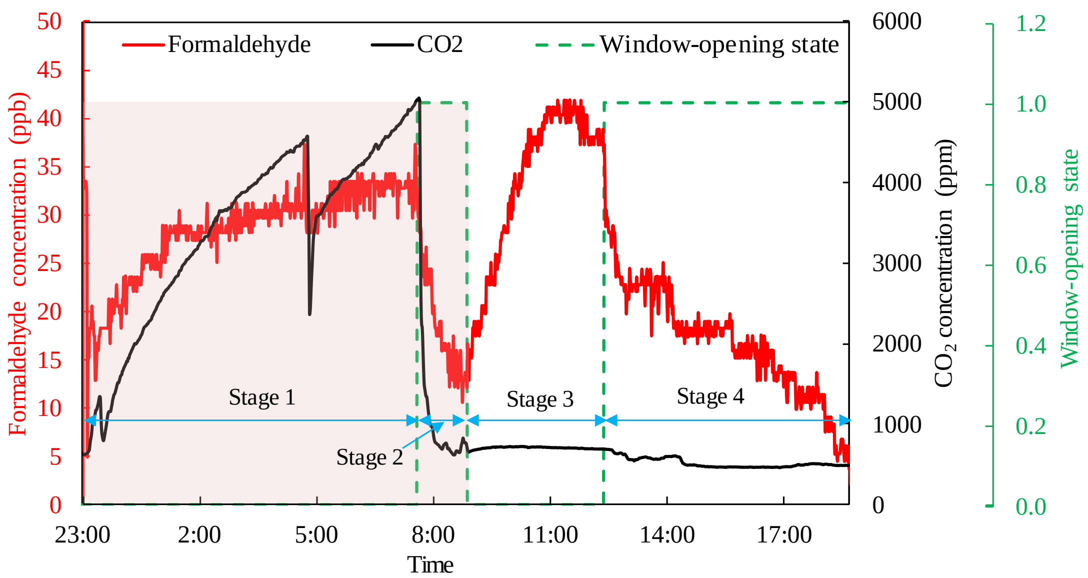


Figure S13. Indoor CO_2 and formaldehyde concentrations in a naturally ventilated dormitory with different window-opening states. The pink zone is the period when the dormitory was occupied; “0” represents a window-closed state and “1” represents a window-open state.

When the room was occupied and the window was closed (stage 1), the indoor CO_2, formaldehyde increased simultaneously. The Pearson correlation coefficients between

CO_2 and formaldehyde was 0.84, indicating strong correlations. When the window was closed and the room was not occupied (stage 3), the CO_2 and formaldehyde concentrations varied differently, resulting in poor correlations with Pearson correlation coefficients of 0.34. When the window was opened, the indoor concentrations of CO_2 and formaldehyde decreased, and they were strongly correlated if the initial concentrations were higher than the outdoor concentrations. The measured correlations were consistent with those of the simulation results.

Reference

Cheng, P. 2018. Natural ventilation rate distribution in dwellings in China's 4 major cities. PhD Dissertation, Tsinghua University, China.

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