Supporting Information for

Application of a new UAV measurement methodology to the quantification of CO_2 and CH_4 emissions from a major coking plant

Tianran Han[1], Conghui Xie[1], Yayong Liu[1], Yanrong Yang[1], Yuheng Zhang[1], Yufei Huang[1], Xiangyu Gao[2], Xiaohua Zhang[3], Fangmin Bao[4], Shao-Meng Li[1]

[1] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, P.R. China
[2] Beijing Wisdominc Technology Co., Ltd., Beijing, P.R. China
[3] Suzhou Environmental Monitoring Center, Jiangsu Province, P.R. China
[4] Jiangsu Shagang Group Co., Ltd., Beijing, P.R. China

Correspondence to: Shao-Meng Li (shaomeng.li@pku.edu.cn)

Section SI-1. TERRA-based determination of CH_4 and CO_2 emission rates

CH_4 and CO_2 emission rates for the surveyed coking plant were determined using the Top-down Emission Rate Retrieval Algorithm (TERRA)(Gordon et al., 2015), which computes integrated mass fluxes through airborne virtual box/screen measurements including those made from aircraft and in this case UAVs. To run TERRA based on a virtual box flight, the first step is to map the CH_4 and CO_2 mixing ratio data measured along the level flight tracks encircling a facility to the two-dimensional virtual walls of the virtual box, created from stacking the level flight tracks, that surrounds the facility. The two-dimensional virtual walls (or screens) are derived from the unwrapping of the virtual box, to assist the presentation of the CH_4 and CO_2 plumes along the flight tracks, with the horizontal path length (i.e., the ground line projection of the fitted flight track) and altitude as the two dimensions. The start of the horizontal path is typically defined as the south-east corner of the virtual box, but the selection of this starting position has no effect on the emission rate computation, and the horizontal path distance increases in a counter clockwise direction. Subsequently, TERRA applies the Simple Kriging algorithm to interpolate the data and produces a mesh on the virtual box walls whose resolution can be set depending on applications, e.g., at 20 m (vertical) by 40 m (horizontal) for aircraft measurements. For the modified version of TERRA applied to the UAV measurements in this study, the mesh has been adjusted to a size of 1 m (vertical) by 2 m (horizontal), as UAVs fly significantly shorter distances compared to piloted

aircraft. The mixing ratios of both CH_4 and CO_2 are extrapolated from the lowest flight altitudes to the ground digital elevation using one of several methods or a combination thereof, namely (1) assuming a constant (2) linear extrapolation between a constant and background (3) a background value below flight altitudes (4) linear fit between the lowest flight altitude and zero at the ground and (5) exponential fit from the lower flight altitudes(Gordon et al., 2015). In this study, CH_4 was extrapolated to the ground mostly using linear and exponential fits that best describe the vertical mixing of ground-based plumes such as emission of CH_4. Concurrently measured wind speed from the UAV(Yang, 2023) is decomposed into two components (parallel and normal to the flight tracks) based on the wind direction and similarly interpolated onto the 1 m x 2 m mesh. The decomposed wind speeds are further extrapolated to the ground digital elevation using a log profile fit(Gordon et al., 2015). Based on the interpolated/extrapolated CH_4 and CO_2 mixing ratio, temperature, pressure, and wind speeds, TERRA computes the fluxes of CH_4 and CO_2 through the virtual walls and finally their facility emission rates by integrating the fluxes.

To summarize, in TERRA the mass-balance in computing the emissions within a control box for a given inert pollutant such as CH_4 or CO_2 is presented by:

$$E_C = E_{C,H} + E_{C,V} - E_{C,M} \quad (1)$$

where E_C is the emission rate, $E_{C,H}$ is the horizontal advective transfer rate through the box walls, $E_{C,V}$ is the advective transfer rate through the box top and $E_{C,M}$ is the increase in mass within the volume due to a change in air density. The vertical transfer rate term $E_{C,V}$ is estimated by computing the air mass vertical transfer rate, determined from vertical wind estimated from air mass balance within the box, and multiplying it with the CO_2 or CH_4 mixing ratios at the box top. This term is normally negligible in top-down emission estimate approaches since it is typically miniscule compared to horizontal fluxes, but can affect the computed emission rates when vertical air movement becomes more significant such as under unstable atmospheric conditions. $E_{C,M}$ is often ignored in other mass-balance approaches; in TERRA it is estimated by taking the time derivative of the ideal gas law in temperature and pressure during the flight time, and typically it does not change significantly over the duration of 30 minutes or so for the UAV flight.

TERRA has been updated at Peking University now with an embedded routine to automatically fit flight tracks, a critical first step in the computation and a procedure previously conducted offline through geographic information system (GIS) when using TERRA. The updated algorithm is now recoded using the Python language and runs under a browser-server environment with a new GUI and new interactive data flow. This updated algorithm is named the Mass Emission and Transfer Rate Evaluation System (METRES) and is copyrighted.

Section SI-2. Uncertainty estimation

To determine the overall uncertainty in the emission rates, each source of uncertainty contributing to the overall uncertainty needs to be identified and quantified. For the emission rate quantification from UAV measurement, the sources of uncertainties include: measurement uncertainties in the mixing ratios and wind speeds (δ_M), the near-surface wind extrapolation (δ_{Wind}), the near-surface mixing ratio extrapolation (δ_{Ex}), box-top mixing ratio (δ_{Top}), box-top height (δ_{BH}) and uncertainties due to data deconvolution as shown in the main text (δ_{Deconv}). Each uncertainty is treated as an independent estimate, and all uncertainties are propagated in quadrature to determine the overall uncertainty in the estimated emission rate:

$$\delta^2 = \delta_M^2 + \delta_{Wind}^2 + \delta_{Ex}^2 + \delta_{Top}^2 + \delta_{BH}^2 + \delta_{Deconv}^2 \quad (2)$$

CH_4 and CO_2 measurement uncertainties from the instrument are <1%. In a previous study(Gordon et al., 2015), a Monte Carlo simulation was used to demonstrate that the uncertainties due to wind speed and mixing ratio measurement uncertainty are both approximately 1%. The uncertainty for wind speed extrapolation is also conservatively estimated as $\delta_{Wind} \approx 1$ % for all cases. Due to a lack of near-surface measurements along the box walls, extrapolation of CH_4 and mixing ratios from the lowest flight path (~ 150 m above ground level) to the ground level has been shown to be a source of potentially large uncertainty within TERRA. The magnitude of the uncertainty depends on the nature of the emissions; for example, surface emissions which may not be fully captured by the flight range have higher uncertainties ≈ 20%, whereas elevated stack emissions which are fully captured by the flight range lead to negligible uncertainties of <4% in the emission estimates(Gordon et al., 2015). To estimate uncertainties due to mixing ratio extrapolation, results from other extrapolation techniques (i.e., linear to

the ground, constant value to the ground, linear to background value, or some combination of methods) were derived and compared with the result from background below flight extrapolation.

Additional components contributing to uncertainties specific to box approach include box-top mixing ratio (δ_{Top}) and box-top height (δ_{BH}). The TERRA box approach assumes a constant mixing ratio at the box top by averaging the measured value at the top level. The term δ_{Top} is determined from the 95% confidence interval ($2\sigma/\sqrt{n}$) of the interpolated measurements. The uncertainty due to the choice of box height, δ_{BH}, within TERRA is estimated by recalculating the emission rate with a reduced box height of 100 m. For cases that use the air sampling system instead of online measuring instruments, as the CH_4 and CO_2 time series measured from the air sampler were deconvoluted to restore the unsmoothed time series before being input into the TREEA algorithm, it is necessary to account for the uncertainty that comes from such deconvolution as outlined in the main text. Time series before and after deconvolution were applied to the TERRA algorithm to obtain the total emission rates, calculation shows that emission rates before and after deconvolution vary within 1%. To this end, the uncertainty for time series deconvolution is conservatively estimated as $\delta_{Wind} \approx 1$ %. The assessment of uncertainties for the TERRA-computed emission rates from the coking plant are listed in Table S1.

Table S1. Assessment of percent uncertainties for CH_4 and CO_2 emission estimations from the two coking plant stacks

	CH_4 (%)	CO_2 (%)
δ_M	1	1
δ_{Wind}	1	1
δ_{Ex}	2	6
δ_{Top}	8	3
δ_{BH}	8	16
δ_{Deconv}	1	1
δ	12	17

Section SI-3. Evaluation of CO_2 emissions through carbon material balance

Figure S1 illustrates the coking process flow and the structure of a coking oven. Coking is a process in which coking coal is heated in an oxygen-free environment to produce coke, a high-carbon metallurgical coke used in steel production. The process takes place in a coke oven, where coking coal is heated at temperatures exceeding 1000 degrees Celsius, driving off all volatile components of the coal and leaving behind coke. Coke oven gas (COG), the byproduct of coking, is mainly composed of the components listed in Table S2(Razzaq et al., 2013). This gas is recovered and mostly reused as the fuel in firing the coke oven to maintain the high temperatures needed for coking(Zhang, 2019), reducing/eliminating the need for external fuel sources. However, burning COG generates CO_2, which is the primary waste gas emitted.

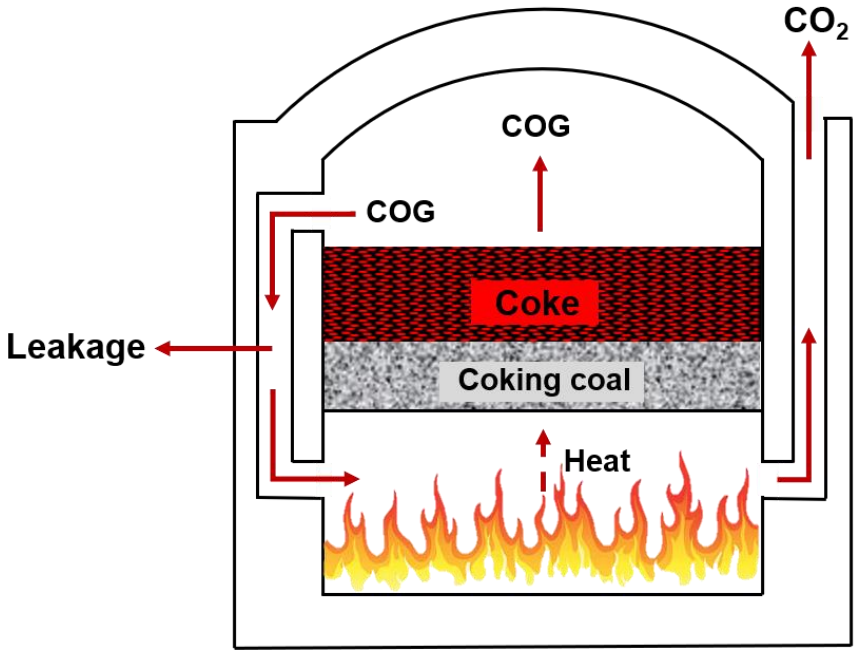

Figure S1. The conceptual coking process flow and the structure of the coking oven

Table S2. Main carbon constitutes and their corresponding compositions (vol%) in coke oven gas

Component	Content
CH_4	23~27%
CO_2	1.5~3%
CO	5~8%
C_2H_4	2~4%

The main products of coking are coke, COG, and slag. In Chinese coking plants(Zhang, 2019), typically half of the produced COG is used as fuel in firing the coke oven, while a small portion is recycled for producing chemical products, and the rest is either leaked (5%)(Hein, 2012) or an unknown fraction is directly released into the atmosphere. The Shagang coking plant has implemented a process for recycling slag. This process involves reusing the slag, which is generated during the coking process, as part of the fuel for the coking oven. As a result, the carbon in the slag is similarly oxidized into CO_2 and subsequently released into the atmosphere as well. Therefore, the CO_2 emissions (E_{co_2}) mainly come from the combustion of COG ($E_{\mathrm{combustion-COG}}$), the combustion of slag ($E_{\mathrm{combustion-slag}}$), and the direct release of COG (E_{release}):

$$E_{co_2} = E_{\mathrm{combustion-COG}} + E_{\mathrm{combustion-slag}} + E_{\mathrm{release}} \quad (3)$$

Based on the carbon material balance, the amount of carbon in COG combusted in the coking oven ($C_{combustion-COG}$) during the coking process can be derived from material balance:

$$C_{combustion-COG} = \alpha(C_{coal} - C_{coke} - C_{slag}) \quad (4)$$

where C_{coal} is the amount of carbon in coal, C_{coke} the amount in coke, and C_{slag} the amount in slag. α is the fraction of COG used in firing the coking oven and is 0.5 based on operation data at the Shagang coking plant. The measured coking plant consists of two coke oven batteries, each with its own stack. Each coking oven battery produced 127.8 t coke hr^{-1}, thus totalling 255.6 t coke hr^{-1} (p_{coke}) between the two batteries during the UAV measurement period with a coke yield of 78.5%. The carbon content of coking coal typically ranges from 80% to 87%(Dai et al., 2022). Assuming an average value of 83.5%, the total amount of carbon in the coking coal used by the coking plant per hour can be calculated as:

$$C_{coal} = \frac{p_{coke}}{78.5\%} \times 83.5\% = 272\ t\ C\ hr^{-1} \quad (5)$$

according to the US EPA, metallurgical coke has a carbon content of 82 to 87%(U.S. Environmental Protection Agency, 2008). If an average value of 84.5% is taken, the produced carbon in the coke during the coking process can be calculated as:

$$C_{coke} = p_{coke} \times 84.5\% = 216\ t\ C\ hr^{-1} \quad (6)$$

Generally speaking, the yield of slag is 0.05% to 0.07% of the coal charged for coking process (an average value of 0.06% is taken here), and that the carbon content of slag is around 80%(Li, 2022). Thus, the total amount of carbon in the produced slag can be calculated as:

$$C_{slag} = \frac{p_{coke}}{78.5\%} \times 0.06\% \times 80\% = 0.16\ t\ C\ hr^{-1} \quad (7)$$

by substituting Eq. (5), (6) and (7) into Eg. (4), the mass of carbon in the combusted COG ($C_{combustion-COG}$) during the coking process is calculated to be 27.9 t hr^{-1}. Thus, $E_{\text{combustion}-\text{COG}}$ and $E_{\text{combustion}-\text{slag}}$ can be calculated respectively:

$$E_{\text{combustion}-\text{COG}} = C_{combustion-COG} \times \frac{M_{CO_2}}{M_C} = 102.3\ t\ CO_2\ hr^{-1} \quad (8)$$

$$E_{\text{combustion}-\text{slag}} = C_{slag} \times \frac{M_{CO_2}}{M_C} = 0.59\ t\ CO_2\ hr^{-1} \quad (9)$$

where M_{CO_2} and M_C is the molar mass of CO_2 and the atomic mass of carbon, respectively.

As certain amount of CO_2 is directly released into the atmosphere along with COG, the carbon mass in the released and measured CO_2 ($C_{release}$) can be derived as:

$$C_{release} = \beta\left(C_{coal} - C_{coke} - C_{slag}\right) \times \frac{\varphi_{CO_2}}{\varphi_{CO_2}+\varphi_{CH_4}+\varphi_{CO}+2\varphi_{C_2H_4}} = 0.16\ t\ hr^{-1} \quad (10)$$

where β is fraction of COG that is directly released into the atmosphere, taken to be 0.05 as described above, φ_{CO_2}, φ_{CH_4}, φ_{CO}, and $\varphi_{C_2H_4}$ are the volume fractions for the main constituents in COG (Table S2). Thus, the corresponding CO_2 emissions from the direct release of COG (E_{release}) cen be derived as:

$$E_{\text{release}} = C_{release} \times \frac{M_{CO_2}}{M_C} = 0.59\ t\ CO_2\ hr^{-1} \quad (11)$$

by substituting Eq. (8), (9) and (10) into Eq. (3), the total CO_2 emissions (E_{co_2}) from the full coking process is calculated to be 103 t CO_2 hr^{-1}.

Taking into account the variation in carbon content found in both coking coal and coke, the variation in the fraction of COG used as fuel (assuming a range of 0.4 to 0.6), the uncertainty of slag yield, as well as the range in the volume fraction of the main components of COG, the total uncertainty range of CO_2 released into the atmosphere during the coking process can be estimated to be 31% by the equation below:

$$\delta^2 = \delta^2_{C_{coal}} + \delta^2_{C_{coke}} + \delta^2_{COG\ as\ fuel} + \delta^2_{slag\ yield} + \delta^2_{volume\ fraction} \quad (12)$$

Thus, the total amount of CO_2 released into the atmosphere during the full coking process estimated from the coke production data is 103±32 t CO_2 hr^{-1}, which is consistent with the CO_2 emission results (110±18 t CO_2 hr^{-1}, see main text) from the current UAV-measurements.

References

Dai, X., Li, D., Li, P., Liu, Y., Guo, D., Zhao, P., and Zhang, Y.: Characterization of microscopic structure and analysis of coking process for various coking coals, Ironmaking & Steelmaking, 1-5, 10.1080/03019233.2022.2102886, 2022.

Gordon, M., Li, S. M., Staebler, R., Darlington, A., Hayden, K., O'Brien, J., and Wolde, M.: Determining air pollutant emission rates based on mass balance using airborne measurement data over the Alberta oil sands operations, Atmospheric Measurement Techniques, 8, 3745-3765, 10.5194/amt-8-3745-2015, 2015.

Hein, M. K., Manfred: Environmental Control and Emission Reduction for Coking Plants, 10.5772/48275, 2012.

Li, J. L., P,; She, X.; Tu, Z.; Wang, J.; Xue, Q.: Pyrolysis and kinetic analysis of tar residue, Modern Chemical Industry, 42, 108-118, 10.16606/j.cnki.issn0253-4320.2022.S2.024, 2022.

Razzaq, R., Li, C., and Zhang, S.: Coke oven gas: Availability, properties, purification, and utilization in China, Fuel, 113, 287-299, 10.1016/j.fuel.2013.05.070, 2013.

U.S. Environmental Protection Agency (EPA): 12.2 Coke Production Final May. https://www.epa.gov/sites/default/files/2020-11/documents/c12s02_may08.pdf, 2008

Yang, Y.: A UAV based 3-D wind measurement methodology for applications to air pollutant emission quantification, in preparation for submission to Environmental Science and Technology, 2023.

Zhang, Y.: Review on the Current Status of Coke Oven Gas Utilization in China, Shandong Chemical Industry, 48, 172-173, 10.19319/j.cnki.issn.1008-021x.2019.16.072, 2019.