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Simulated reaction of formaldehyde and ambient atmospheric particulate matter using a chamber

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ABSTRACT

The reaction of HCHO with Beijing winter's real ambient particulate matter (PM) inside a 3.3 m³ Teflon Chamber was conducted in this study. NO₂, O₃ and H₂O gases were removed from the ambient aerosol before entering into the chamber. The decays of HCHO were monitored (acetylacetone spectrophotometry method) during the reactions at different PM number concentrations (N_a) and relative humidities (RHs), and the formed particulate formate was detected by IC and XPS techniques. The results showed that when RH was 10%–15%, the decay rate of HCHO in the chamber was higher with the existence of PM from relatively clean days (with number concentration (N_a) < 200,000 particle/L, 0.35–22.5 μm) compared to dirty days (N_a > 200,000 particle/L, 0.35–22.5 μm). When RH increased to 30%–45%, PM can hardly have significant influences on the decay of HCHO. The formations of formate on the reacted PM were consistent with the HCHO decay rates at different ambient PM N_a and RH conditions. This is a first study related to the “real” ambient PM reacted with HCHO and suggested that in the clean and low RH days, PM could be an effective medium for the conversion of HCHO to formate.

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Introduction

Volatile organic compounds (VOCs), key constituents in the atmosphere, play important roles in the formation and aging of fine particulate matter (PM). It can react with oxidizing gases (*e.g.*, ozone) and radicals (*e.g.*, OH and HO₂ radicals), contributing to the growth of fine PM. VOCs may even go through heterogeneous reactions with substances on PM, which enhances particle growth and changes the chemical composition of particles as well as the physical properties, *e.g.*, hygroscopicity and optical properties (Liggio *et al.*, 2005).

Formaldehyde (HCHO) is the most abundant carbonyl-containing VOCs in the atmosphere, and has a strong reducibility (Possanzini *et al.*, 2002; Liu *et al.*, 2015). HCHO in the atmosphere

comes from the oxidation of organic compounds or the direct emitting from combustion and industrial sources (Seinfeld and Pandis, 2006). The reaction with OH radicals, photolysis, and dry or wet deposition are well known as its removal pathways. Recently, the heterogeneous processes between HCHO and aerosols, *e.g.*, sulfate aerosols (Jayne *et al.*, 1996; Iraci and Tolbert, 1997), mineral dust aerosols (Carlos-Cuellar *et al.*, 2003; Xu *et al.*, 2006, 2010; Hatch *et al.*, 2007; Sassine *et al.*, 2010), and organic aerosols (Li *et al.*, 2011), were found to contribute to the destruction of HCHO, providing additional sinks for HCHO (Hatch *et al.*, 2007). Among those researches, mineral dust aerosols were explored most, such as SiO₂, TiO₂, α-Al₂O₃ and α-Fe₂O₃. The adsorptions of HCHO by α-Al₂O₃, α-Fe₂O₃ and TiO₂ were found to be irreversible and formate was revealed as the most important

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and abundant product during the reaction (Carlos-Cuellar et al., 2003; Xu et al., 2006), which may affect the hygroscopicity and optical properties of particles (Hatch et al., 2007). In addition, meteorological factors, *e.g.*, temperature, relative humidity (RH) and light radiation, also affect the heterogeneous reactions of VOCs (Shen et al., 2013).

However, the reaction of formaldehyde with ambient PM has not been studied yet. Monocomponent particles, though frequently used in current studies, cannot reflect the situation in real atmosphere. Ambient PM usually goes through an aging process in the atmosphere and become multicomponent and complicated, making it different from the simulated particles in laboratory experiment (Shen et al., 2013). Additionally, under different pollution conditions, ambient PM tends to appear with different chemical compositions, which will directly affect its reactivity in the atmosphere and its physiochemical characteristics change afterwards (Khalizov et al., 2010; Sun et al., 2013a, 2013b).

Beijing, the political center and one of the megacities in northern China, has been suffering from heavy air pollution during the last two decades (Chen et al., 2007). According to the data from Beijing Environmental Statement, the annual average mass concentration of PM_{2.5} in Beijing was 89.5 and 85.9 $\mu\text{g}/\text{m}^3$ in 2013 and 2014 respectively (Sun et al., 2015), over 2 times of annual average of 35 $\mu\text{g}/\text{m}^3$ in the National Ambient Air Quality Standard. The occurrence frequency of severe air pollution was quite different in different seasons in Beijing throughout the year. Winter, with heating process and special weather conditions, has typically heavier air pollution than in other seasons in Beijing (Sun et al., 2013a, 2013b). The compositions of PM on those polluted days are also changing in different seasons, *e.g.*, PM in winter pollution period tends to possess larger mass fraction of secondary organics (Liu et al., 2012; Cheng et al., 2015).

Facing with the above problems, this study conducted the reaction of HCHO and ambient PM gathered from different polluted-level days in the winter of Beijing via an indoor environmental chamber. This is the first work using “real” ambient PM as interface to investigate the potential impact that complex ambient PM may have on the decay of HCHO. The decay rate of HCHO, the generated formate on the particles, the surface characteristics and the changes of element content on particles were analyzed and the impact of humidity on the process was explored.

1. Materials and methods

1.1. Reaction chamber set-up

Schematic of the indoor chamber is illustrated in Fig. 1. It is a 3.3-m³ Teflon bag (Plastic research institute of Shanghai, China) with a side length of 1.5 m, located on the third floor in the building of the College of Environmental Sciences and Engineering in Peking University, Beijing, China (116.3°E, 40.0°N). Experiments performed in the chamber were mainly conducted on winter days from Nov. 2013 to March 2015. An air blower (FLS-11; Fulanshi, China) with a flow of 41.6 L/min was used to introduce ambient PM into the chamber. Before

entering into the chamber, the gas flow of ambient air was passed through three serial denuders filled with silica gel, KOH and KI (Analytical reagent; Tianjin Zhiyuan Chemical Reagent, Tianjin, China) sequentially. These denuders decreased 56%, 90% and 67% the levels of water vapor, NO₂ and O₃ in ambient air, respectively (Liu, 2015). PM concentration in the chamber was kept relatively constant by varying introduction time. Each time before experiment, the chamber went through a cyclic cleaning by particle-free clean air generated from ambient air where a particle filter (Oil-X Evolution efficient compressed air filter, ACS010BBMX; Parker Domnick Hunter, UK) was used to remove ambient PM along with the above described denuders. RH in the chamber was controlled by bubbling water system with clean particle-free air. An RH of 10%–15% is adopted in most of the chamber experiment but a higher RH of 30%–45% was used when estimating the impact of RH changes. A thermohygrometer (HD 2301.0, Delta OHM, Italy) with a sensor probe (HP 474 AC, Delta OHM, Italy) was used to measure RH and temperature in the chamber. All the chamber experiments were conducted under the temperature of 288 K. A Shade cloth was used to shade the chamber from sunlight radiation.

Wall effects of the chamber for PM and HCHO were both evaluated before all the chamber experiments, where ambient PM or HCHO was introduced into the chamber respectively (the latter is described later in Section 1.2). In the reaction experiment, HCHO was introduced into the chamber after PM and the reaction timing started after a 10–15 min mixing time. The number concentration of PM in chamber was recorded and the loss rate of PM was calculated. For HCHO, the decay rate was calculated according to its concentrations varying over time (see Section 1.4).

1.2. HCHO generation and detection

A pyrolysis method according to Xu et al. (2006) was adopted to generate gaseous HCHO. Powdery paraformaldehyde (purity 95%; J&K Scientific, Beijing, China) was placed in self-made glassware and heated under a temperature of 343 K in water bath. A constant flow of N₂ (0.08 L/min) was introduced into the glassware to carry high-purity gaseous HCHO into the chamber. The initial concentration levels of HCHO in chamber were controlled by varying the time of gas introduction and measured by acetylacetone spectrophotometry (Wang and Lu, 2004). In the acetylacetone spectrophotometry method, a constant flow of HCHO (0.16 L/min) from the chamber was absorbed by deionized water (10 mL) in a porous sieve-plate tube, followed by measuring the absorbance at 412 nm with a spectrophotometer (T6 UV-Vis; Purkinje, China) after the introduction of acetylacetone and a boiling water bath. The concentration of HCHO in the chamber was derived according to the absorbance and a standard curve. The standard curve was obtained at the beginning of the reaction experiment, as shown in Eq. (1),

$$A = 0.0003C + 0.0009 \quad (R^2 = 0.9989) \quad (1)$$

where, A denotes the absorbance of HCHO at 412 nm and C is the concentration (ppm) of HCHO.

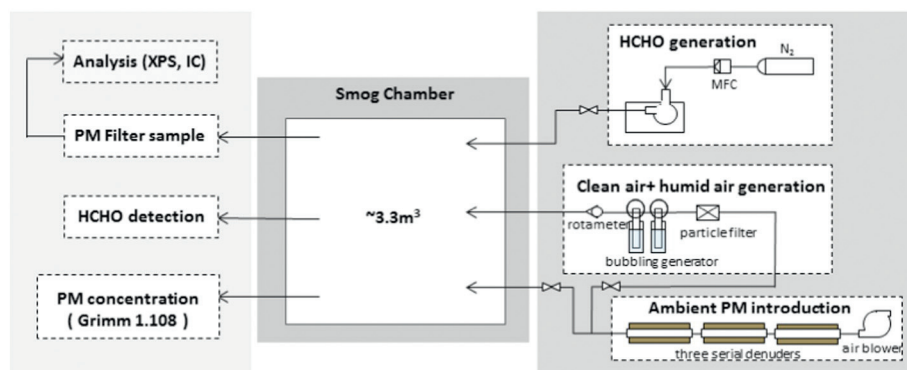


Fig. 1 – Schematic of the indoor environmental chamber.

1.3. Particle monitoring, collection and characterization

Before and after reaction, several methods are used to measure the PM concentration, element and organo-functional group components of PM and formate concentration on the surface of PM. The particle number concentration (particle/L, hereinafter, N_a) and mass concentration (mg/m^3 or $\mu\text{g}/\text{m}^3$; hereinafter, C_a) were both monitored by a portable aerosol spectrometer Grimm1.108 (Grimm Aerosol Technik, GmbH & Co. KG, Ainring, Germany) at a flow rate of 1.2 L/min. Employing a semiconductor laser as light source, Grimm1.108 measures the number of particles per unit volume of air via light scattering technology. It can measure particles with an optical size range from 0.35 to 22.5 μm and concentration range of 1–2,000,000 particle/L or mass concentration range of 0.001–100 mg/m^3 . Ambient PM in the chamber after reaction was collected at a flow rate of 37.5 L/min by quartz filters (pore diameter 0.45 μm , 47 mm; Pall Life Sciences, USA) placed within a Teflon holder. Quartz filters were heated above 823.15 K for 6 hr and then balanced for over 24 hr under constant temperature and humidity before sampling. Filters loaded with PM were stored at 253.15 K refrigerator in dark for follow-up chemical characterizations.

Element components and energy bands of PM were analyzed by X-ray photoelectron spectroscopy (XPS; Axis Ultra, Kratos Analytical Ltd., USA) and Casa XPS software was used to perform data analysis. The concentration of formate on PM surface was measured by ion chromatography (IC; ICS-2000, Dionex, USA), where deionized water was used to extract PM from filters and also as the eluent in IC.

1.4. HCHO decay rate evaluation

To estimate the impact of ambient PM on the decay of HCHO, it is necessary to examine the net decay rate of HCHO without the existence of ambient PM first, i.e., the wall loss of HCHO in the chamber. Particle-free clean air and HCHO were introduced into the chamber successively. After a mixing time of 15 min, the concentration of HCHO was measured in every 15 min. The decay of HCHO in chamber fits a Pseudo first-order kinetics equation,

$$C = C_0 e^{-k_0 t} \quad (2)$$

where, C (ppm) and C_0 (ppm) stand for the concentration of HCHO at t moment and initial concentration, k_0 is the decay rate of HCHO without ambient PM existing in the chamber.

When evaluating the influences of ambient PM on the decay rate of HCHO, ambient PM was introduced into the chamber with cleaned ambient air following the introduction of HCHO. Then the HCHO concentration was measured. In this case, k_0 in Eq. (2) is replaced by k_p , which means the decay rate of HCHO with ambient PM existing.

2. Results and discussion

2.1. Decay rate of HCHO in the chamber

2.1.1. Wall loss effect of HCHO in the chamber

As mentioned above, the decay rate of HCHO (k_0) with different C_0 ranging from 2 to 22 ppm under the RH of 10%–15% was measured. Here, one of a typical HCHO concentration versus time curve is illustrated in Fig. 2 at that C_0 is 22 ppm and k_0 is 0.0121/min. Considering the wall loss effect of HCHO in the chamber, k_0 was measured in every chamber experiment and $(k_p - k_0)$ is calculated and used to evaluate the impact of ambient PM on the decay rate of HCHO (see Section 2.1.2).

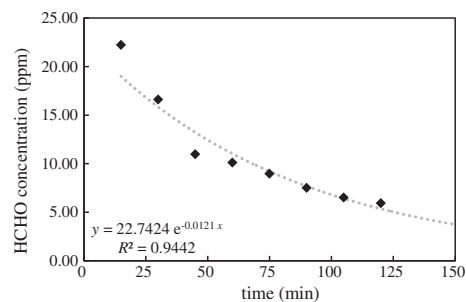


Fig. 2 – Variation of HCHO concentrations with time in the chamber without PM at $C_0 = 22$ ppm, RH: 10%–15%, temperature: 288 K. PM: particulate matter; RH: relative humidity.

2.1.2. Impact of ambient PM on the decay rate of HCHO

Under a constant initial concentration of HCHO around 10 ppm, the impact of ambient PM on the decay of HCHO in the chamber was evaluated by calculating $(k_p - k_0)$ for PM number concentration (N_a) varying from 10,000 to 1,060,000 particle/cm³ in the chamber (Fig. 3). The larger the value is above zero, the bigger the impact is. Given the huge discrepancy on PM number concentrations and to illustrate the data in a clearer way, $\log(N_a)$, the logarithm of number concentration of PM, was used to identify PM for different polluted days. In Fig. 3, a negative correlation between $(k_p - k_0)$ and $\log(N_a)$ was revealed. Additionally, $(k_p - k_0)$ is above zero when $\log(N_a)$ is less than 5.3, hence $\log(N_a) = 5.3$ (corresponding $N_a = 200,000$) can be regarded as a cutting line. Hereinafter, days with $\log(N_a)$ above 5.3 is described as relatively dirty days (DD) and days with $\log(N_a)$ below 5.3 is described as relatively clean days (CD). A further significant analysis was made by Statistical Product and Service Solutions (SPSS) statistics version 22. Paired-sample t-test was adopted after logarithm transformation and normal distribution test of the data. The test result shows that significant differences exist between k_p and k_0 when $\log(N_a)$ is less than 5.3 (significance level p -value = 0.014 < 0.05), while the opposite is not (significance level p -value = 0.804 > 0.05). Hence, the data in Fig. 3 demonstrates that PM from CD contributes more to the decay of HCHO, while PM from DD seems to slow down the decay of HCHO.

2.2. Particulate formate formation

Xu et al. (2006) have studied the heterogeneous reaction of formaldehyde with α -Al₂O₃ by using in-situ diffuse reflectance infrared Fourier transform spectroscopy. Their study confirmed that HCHO can be oxidized firstly to dioxymethylene by reactive oxygen species and then formate. In this study, the mass percent of formate on PM was measured by IC and recorded as P_0 and P_f , respectively before and after HCHO exposure. Fig. 4 denotes the growth of formate measured on PM after exposure to HCHO. As revealed in Fig. 4, $(P_f - P_0)$ declines as $\log(N_a)$ increases, which means that less formate is found on PM from DD than from CD after HCHO exposure. Comparing Figs. 3 and 4, that relation of $(P_f - P_0)$ and $\log(N_a)$ shares similar trend with that of $(k_p - k_0)$ and $\log(N_a)$. Therefore, it may be stated that PM from CD accelerates the decay of HCHO, resulting in larger generation of formate.

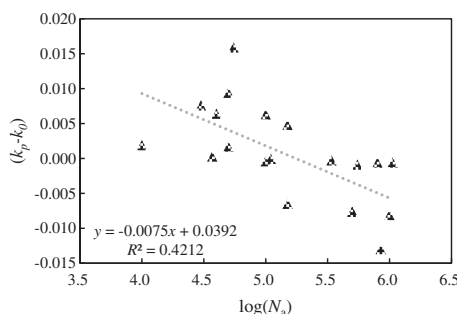


Fig. 3 – Decay rate of HCHO in the presence of PM with different N_a at RH: 10%–15%, temperature: 288 K.

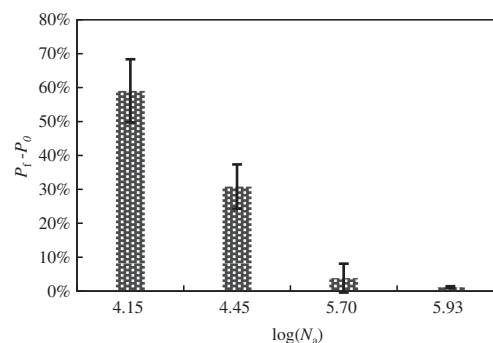


Fig. 4 – The increment of formate production after HCHO exposure for PM with different N_a (RH: 10%–15%, temperature: 288 K).

2.3. XPS analyses of PM before and after reactions

Elemental components of PM from days with different N_a before and after HCHO exposure were analyzed by XPS. Two typical results from CD and DD respectively are illustrated in Fig. 5. Results shown in Fig. 5a, b were from the experiment conducted on Nov. 6th, 2015 when $N_a = 12,589$ ($\log(N_a) = 4.1$), while that in Fig. 5c and d were from the one conducted on Oct. 9th, 2015 when $N_a = 398,107$ ($\log(N_a) = 5.6$). Both Fig. 5a, c show XPS spectra of PM before HCHO exposure while Fig. 5b, d are after HCHO exposure. Quantitative evaluations of the PM surface functional groups were performed by analyzing the C1s bond. Generally, peaks at approximately 284.81–285.03, 286.42–286.73, 287.81–288.03 and 288.60–289.55 eV were attributed to hydrocarbons (C–C, C–H), ethers (C–O), carbonyl group (C=O) and carboxylate groups (O–C=O), respectively (Singh et al., 2014). As shown in Fig. 5, four peaks at 284.8, 285.6, 287.0 and 288.8 eV were observed in each figure after curve fittings of the C1s spectra. More detailed results are displayed in Table 1 where A_0 and A_f are the peak-area fractions of the functional groups before and after HCHO exposure, respectively, and $(A_f - A_0)/A_0$ indicates the net growth of functional groups. As is revealed, the C/O ratio of PM from CD and DD declines from 1.84 to 0.24 and 1.15 to 0.16, respectively, which means a larger fraction of oxygen-containing groups on PM after HCHO exposure. Concretely, the fraction of C=O and O–C=O on PM increased after the interaction with HCHO in the chamber, while the fraction of C–H and C–O declined. Other studies, though using different types of particle samples such as black carbon or biochar, found similar variation tendency for O–C=O functional groups on particles after aging (Cheng et al., 2006; Singh et al., 2014). The results suggest that ambient PM probably went through an aging process in the chamber with the presence of HCHO. Additionally, for PM from DD, the fraction of C=O and O–C=O components was found to hold larger mass percentages but increase less after HCHO exposure, comparing to that of PM from CD (Fig. 5, Table 1). This result coincides with the ones found in Figs. 3 and 4. These phenomena indicate that PM from DD experienced atmospherically aging process resulting in its higher carboxylate compounds but lower reactivity with HCHO, while PM from CD maybe more reactive to HCHO and promotes the transfer of HCHO to formate.

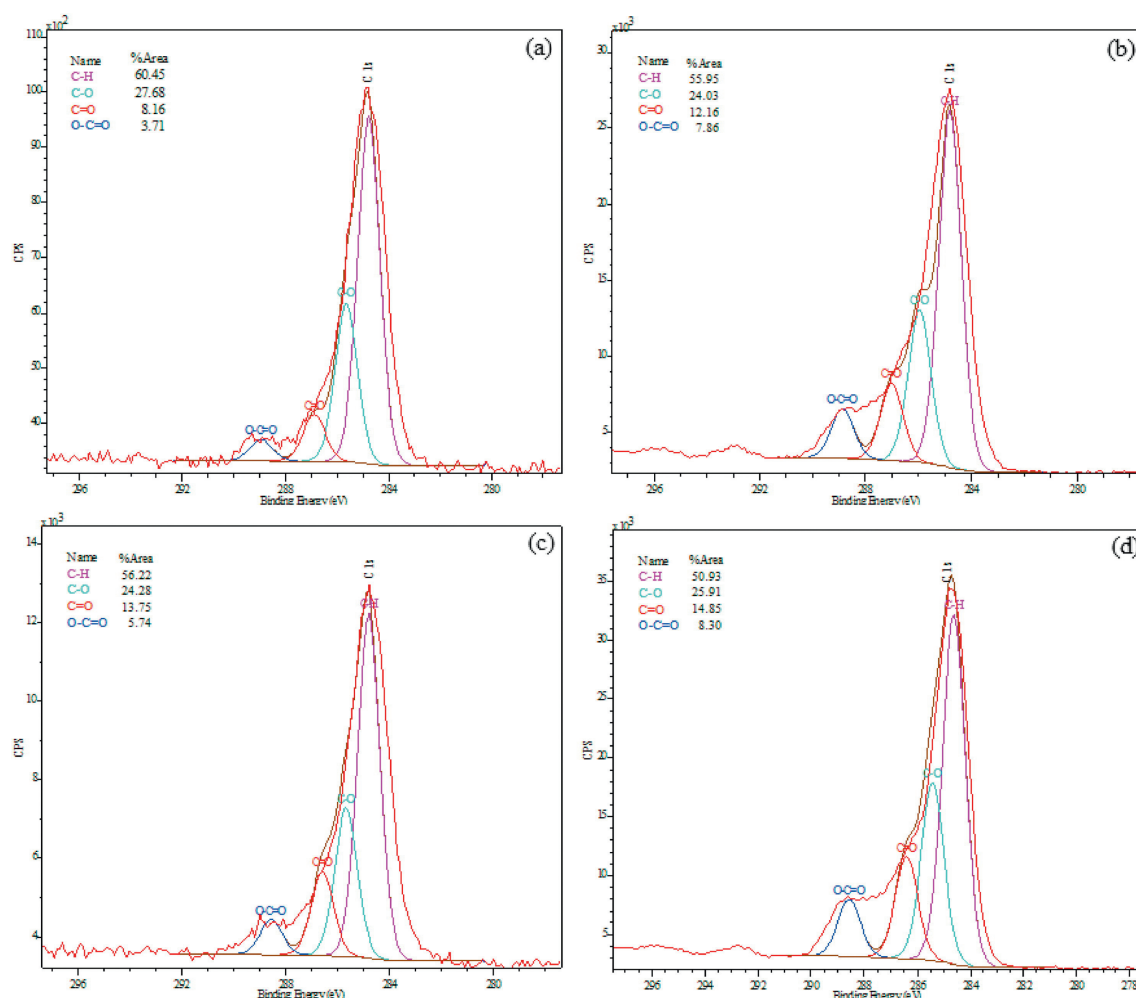


Fig. 5 – XPS spectra of PM from CD ($\log(N_a) = 4.1$) before (a) and after (b) interaction with HCHO; XPS spectra of PM from DD ($\log(N_a) = 5.6$) before (c) and after (d) interaction with HCHO. RHs are all of 10%–15%, and temperature of 288 K. XPS: X-ray photo-electron spectroscopy; PM: particulate matter; CD: clean days; DD: dirty days; RH: relative humidity.

2.4. Effect of relative humidity

Except for RH of 10%–15%, a higher RH of 30%–45% was also tested. By comparing the results of relatively high RH (30%–45%) with low RH (10%–15%), the effect of RH on the decay of HCHO and on the formation of formate on PM after HCHO exposure was explored. As for HCHO decay rate ($k_p - k_0$) shown in Fig. 6, the high level of RH has different impacts on ($k_p - k_0$) considering days with different N_a levels. When RH is increased to 30%–45%, both the inhibiting effect of PM from DD and the acceleration effect of PM from CD on HCHO decay become retarded, nearly losing effects. This was similar with the results of other studies

about mineral aerosol dust (Sassine et al., 2010; Zhang et al., 2006; Singh et al., 2014). For instance, Sassine et al. (2010) observed that the increase of RH from 6% to 70% first enhanced and then at around 30% slowed down the HCHO uptake on particles. It can be explained by the competitive adsorption between water and HCHO or the decreasing amount of reactive oxygen species (ROS) on particle surface (Zhang et al., 2006). As for the formate content, RH in this study showed a similar effect as it on the decay of HCHO. As is shown in Fig. 7, the increase of RH from 10%–15% to 30%–45% generally reduces ($P_f - P_0$). Moreover, ($P_f - P_0$) declines more for PM from days with smaller N_a when RH increases. But, as $\log(N_a)$ becomes larger than 5.3, ($P_f - P_0$) may even increase

Table 1 – The content variation of functional groups on PM from CD and DD after HCHO exposure.

Date for experiment (pollution condition)	$\log(N_a)$	k_0	k_p	$P_f - P_0$ (%)	C/O (before/after)	$(A_f - A_0)/A_0$ (%)			
						C–H, C–C	C–O	C=O	O–C=O
Nov. 6th, 2015 (CD)	4.1	0.0020	0.0023	65.6	1.84/0.24	–7.44	–13.19	49.02	111.9
Dec. 9th, 2015 (DD)	5.6	0.0020	0.0004	1.4	1.15/0.16	–9.41	6.71	8.08	44.6

For $(A_f - A_0)/A_0$ (%), positive value indicates the increase of corresponding functional group content and the vice versa.
PM: particulate matter; CD: clean days; DD: dirty days.

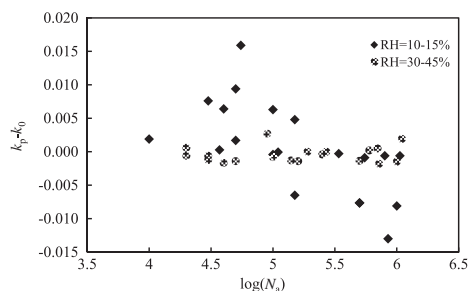


Fig. 6 – The impact of ambient PM with different number concentrations on HCHO's decay rate under different RH. PM: particulate matter; RH: relative humidity.

slightly when RH rises to 30%–45%. That, except for data deviation, might be the results of the increased water uptake on PM. A higher RH facilitates the uptake of water for formic acid on PM surface, which leads to the increase in formate formation (Paulot et al., 2011). Besides, Beijing PM is more hygroscopic at conditions of high PM concentrations during winter (Cheng et al., 2015), which probably further promotes the uptake of water.

3. Conclusions

In this study, ambient PM was introduced into a Teflon chamber to investigate the “real” atmospheric particles' interaction with HCHO. In the condition of RH 10%–15%, PM from Beijing winter relatively CD can promote the decay rate of HCHO, which was further confirmed by the enhanced formation of formate and carbonyl group on the reacted particles; while PM from relatively DD shows no acceleration for the decay rate of HCHO with slightly increased amount of formate and carbonyl group formation. Additionally, when RH in the chamber increased from 10%–15% to 30%–45%, PM hardly presents obvious impact on the decay rate of HCHO, which is also independent of its N_a value. The enhancement of RH generally reduced formate mass fraction on PM from CD. This study provided, so far as we know, a first exploration of reaction between HCHO and real atmospheric PM in a chamber. The enhancement of HCHO decay rates after PM introduction in chamber matched well with that of formate and carbonyl groups formation. These results indicate that

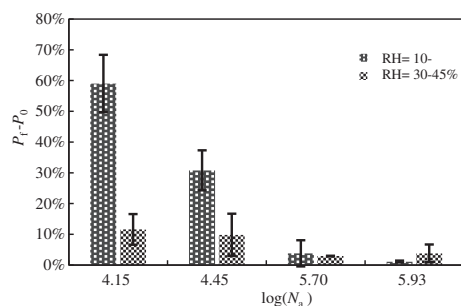


Fig. 7 – The increment of formate on PM from days with different N_a after HCHO exposure under different RH. PM: particulate matter; RH: relative humidity.

ambient PM in relatively clean and low RH days could act as a medium for the conversion of HCHO to formate and the vice versa.

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REFERENCES

- Carlos-Cuellar, S., Li, P., Christensen, A.P., Krueger, B.J., Burrichter, C., Grassian, V.H., 2003. Heterogeneous uptake kinetics of volatile organic compounds on oxide surfaces using a Knudsen cell reactor: adsorption of acetic acid, formaldehyde, and methanol on α -Fe₂O₃, α -Al₂O₃, and SiO₂. *J. Phys. Chem. A* 107 (21), 4250–4261.
- Chen, H., Xia, X.G., Wang, P., Zhang, W.X., 2007. Ground-based measurements of aerosol optical properties and radiative forcing in North China. *China Part 5* (3), 202–205.
- Cheng, Y., He, K., Du, Z.Y., Zheng, M., Duan, F.K., Ma, Y.L., 2015. Humidity plays an important role in the PM_{2.5} pollution in Beijing. *Environ. Pollut.* 197, 68–75.
- Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* 37 (11), 1477–1488.
- Hatch, C., Gough, R., Tolbert, M., 2007. Heterogeneous uptake of the C-1 to C-4 organic acids on a swelling clay mineral. *Atmos. Chem. Phys.* 7 (16), 4445–4458.
- Iraci, L., Tolbert, M., 1997. Heterogeneous interaction of formaldehyde with cold sulfuric acid: implications for the upper troposphere and lower stratosphere. *J. Geophys. Res.-Atmos.* 102 (13), 16099–16107.
- Jayne, J.T., Worsnop, D.R., Kolb, C.E., Swartz, E., Davidovits, P., 1996. Uptake of gas-phase formaldehyde by aqueous acid surfaces. *J. Phys. Chem.* 100, 8015–8022.
- Khalizov, A., Cruz-Quinones, M., Zhang, R., 2010. Heterogeneous reaction of NO₂ on fresh and coated soot surfaces. *J. Phys. Chem.* 114 (48), 7516–7524.
- Li, Z., Schwiier, A.N., Sareen, N., McNeill, V.F., 2011. Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products. *Atmos. Chem. Phys.* 11 (22), 11617–11629.
- Liggio, J., Li, S., McLaren, R., 2005. Reactive uptake of glyoxal by particulate matter. *J. Geophys. Res.-Atmos.* 110 (10), 304.
- Liu, J., 2015. Simulated Heterogeneous Reaction of Formaldehyde and Ambient Particles Using an Environmental Chamber (MD thesis) Peking University, Beijing, China.
- Liu, Q., Sun, Y., Hu, B., Liu, Z.R., Akio, S., Wang, Y.S., 2012. In situ measurement of PM₁ organic aerosol in Beijing winter using a high-resolution aerosol mass spectrometer. *Chin. Sci. Bull.* 57 (7), 819–826.
- Liu, Y., Yuan, B., Li, X., Shao, M., Lu, S., Li, Y., et al., 2015. Impact of pollution controls in Beijing on atmospheric oxygenated volatile organic compounds (OVOCs) during the 2008 Olympic Games: observation and modeling implications. *Atmos. Chem. Phys.* 15, 3045–3062.
- Paulot, F., Wunch, D., Crounse, J.D., Toon, G.C., Millet, D.B., DeCarlo, P.F., et al., 2011. Importance of secondary sources in the atmospheric budgets of formic and acetic acids. *Atmos. Chem. Phys.* 11 (5), 1989–2013.
- Possanzini, M., Di Palo, V., Cecinato, A., 2002. Sources and photodecomposition of formaldehyde and acetaldehyde in Rome ambient air. *Atmos. Environ.* 36 (19), 3195–3201.

- Sassine, M., Burel, L., D'Anna, B., George, C., 2010. Kinetics of the tropospheric formaldehyde loss onto mineral dust and urban surfaces. *Atmos. Environ.* 44 (40), 5468–5475.
- Seinfeld, J.H., Pandis, S.H., 2006. *Atmospheric Chemistry and Physics From Air Pollution to Climate Change*. 2nd ed. Wiley, New York, USA.
- Shen, X.L., Zhao, Y., Chen, Z.M., Huang, D., 2013. Heterogeneous reactions of volatile organic compounds in the atmosphere. *Atmos. Environ.* 68, 297–314.
- Singh, B., Fang, Y.Y., Cowie, B.C.C., Thomsen, L., 2014. NEXAFS and XPS characterization of carbon functional groups of fresh and aged biochars. *Org. Geochem.* 77, 1–10.
- Sun, Y.L., Wang, Z.F., Fu, P.Q., Jiang, Q., Yang, T., Li, J., et al., 2013b. The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. *Atmos. Environ.* 77, 927–934.
- Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., Jiang, Q., Dong, H.B., et al., 2013a. Aerosol composition, sources and processes during wintertime in Beijing, China. *Atmos. Chem. Phys.* 13 (9), 4577–4592.
- Sun, Y.L., Wang, Z.F., Du, W., Zhang, Q., Wang, Q.Q., Fu, P.Q., et al., 2015. Long-term real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis. *Atmos. Chem. Phys.* 15 (17), 10149–10165.
- Wang, S., Lu, D., 2004. Formaldehyde measurement in the indoor air by the method of acetyl acetone with spectrophotometer. *J. Suzhou Inst. Silk Text. Technol.* 23 (6), 15–17.
- Xu, B.Y., Zhu, T., Tang, X.Y., 2006. Heterogeneous reaction of formaldehyde on surface of α - Al_2O_3 particles. *Chem. J. Chin. Univ.* 27 (10), 1912–1917.
- Xu, B.Y., Zhu, T., Tang, X.Y., Shang, J., et al., 2010. Heterogeneous reaction of formaldehyde on the surface of TiO_2 particles. *Sci. China Ser. B* 53 (12), 2644–2651.
- Zhang, C., He, H., Tanaka, K., 2006. Catalytic performance and mechanism of a Pt/ TiO_2 catalyst for the oxidation of formaldehyde at room temperature. *Appl. Catal. B Environ.* 65 (1–2), 37–43.