Physicochemical uptake and release of volatile organic compounds by soil in coated-wall flow tube experiments with ambient air

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Abstract

Volatile organic compounds (VOCs) play a key role in atmospheric chemistry. Emission and deposition on soil have been suggested as important sources and sinks of atmospheric trace gases. The exchange characteristics and heterogeneous chemistry of VOCs on soil, however, are not well understood. We used a newly designed differential coated-wall flow tube system to investigate the long-term variability of bidirectional air-soil exchange of 13 VOCs at ambient air conditions of an urban background site in Beijing. Sterilized soil was investigated to address physicochemical processes and heterogeneous/multiphase reactions independently from biological activity. Most VOCs revealed net deposition with average uptake coefficients (γ) in the range of $10^{-7} - 10^{-6}$ (referring to the geometric soil surface area), corresponding to deposition velocities (V_d) of $0.0013 - 0.01$ cm s^{-1} and soil surface resistances (R_c) of $98 - 745$ s cm^{-1}, respectively. Formic acid, however, was emitted at a long-term average rate of $\sim 6 \times 10^{-3}$ nmol m^{-2} s^{-1}, suggesting that it was formed and released upon heterogeneous oxidation of other VOCs. The soil-atmosphere exchange of one individual VOC species can be affected by both its surface degradation/depletion caused by surface reactions and by competitive uptake or heterogeneous formation/accommodation of other VOC species. Overall, the results show that physicochemical processing and heterogeneous oxidation on soil and soil-derived dust can act as a sink or as a source of atmospheric VOCs, depending on molecular properties and environmental conditions.

1 Introduction

Volatile organic compounds (VOCs) are widely recognized to play a critical role in atmospheric chemistry and climate, because of their important impact on the atmospheric oxidation capacity and contribution to the formation of secondary organic aerosols (SOAs) (Andreae and Crutzen, 1997;Atkinson, 2000;Fuentes et al., 2000;Williams, 2004;Tunved et al.,
5 2006;Lelieveld et al., 2008;Zhang et al., 2008;Pöschl et al., 2010), and VOCs adsorbed on aerosol particles can have severe health implications (Glikson et al., 1995;Pöschl, 2005). The main sources of VOCs include the biosphere, biomass burning and anthropogenic activities, with emissions from the biosphere accounting for ~ 90% of global total atmospheric VOCs (Guenther et al., 1995). Once VOCs are emitted, they can be removed from the atmosphere by either direct wet or dry deposition to various surfaces including vegetation and soil (130 – 270 Tg C yr^{-1}), or be transformed into SOAs (510 – 910 Tg
10 C yr^{-1}), or be oxidized ultimately leading to the formation of CO_2 and H_2O (310 – 720 Tg C yr^{-1}) (Goldstein and Galbally, 2007). The reported discrepancies between field observations and model calculations, however, indicate many potential sources and sinks still need to be identified and quantified (Di Carlo et al., 2004;Heald et al., 2005;Volkamer et al., 2006;Goldstein and Galbally, 2007;Warneck and Williams, 2012).

15 Biogenic VOC emission from vegetation has long been the major focus of VOC exchange studies (e.g., Guenther et al., 1994;Gershenzon, 1994;Fuentes et al., 1996;Fall et al., 1999;Schade and Goldstein, 2002). Early studies presumed that vegetation only emitted VOCs to the air. However, more recent studies have demonstrated that VOC exchange is bidirectional, and uptake of VOCs and their oxidation products are the rule rather than the exception in many cases (Kesselmeier, 2001;Fares et al., 2015;Guenther, 2015;Cappellin et al., 2017;Karl et al., 2005;Seco et al., 2007;Karl et al., 2010;Park et al., 2013;Gordon
20 et al., 2014a;Niinemets et al., 2014), similar to other trace gases such as NH_3 or HONO (Su et al., 2011;Su et al., 2013). In fact, Park et al. (2013) expanded the number of measured VOC species to an extremely large range covering 555 ions (with mass to charge ratios between 31 to 1263) using high–mass resolution proton-transfer-reaction mass spectrometry over an orange plantation, and found that 494 of VOC species showed bidirectional fluxes and 186 even exhibited net deposition.

25 Compared to the research effort dedicated to atmosphere-vegetation interactions involving VOCs, the exchange between the atmosphere and soils has received relatively little attention (Lamb et al., 1987;Guenther et al., 1995;Asensio et al., 2008). Soils have been characterized as both a source and a sink for VOCs. Soil emissions of short-chain oxygenated VOCs (e.g., methanol, acetaldehyde and acetone) and terpenes have been observed in previous studies (Warneke et al., 1999;Schade and Goldstein, 2001;Hayward et al., 2001;Schade and Custer, 2004;Lin et al., 2007;Gray et al., 2014;Bourtsoukidis et al., 2018). In contrast,
30 some species including alcohols, aldehydes, ketones, aromatic hydrocarbons, isoprene, monoterpenes and hexenal, etc. have been reported to be deposited on various types of soil in other studies (Asensio et al., 2007a;Asensio et al., 2007b;Asensio et al., 2008;Aaltonen et al., 2013;Gray et al., 2014). Previous laboratory measurements have also indicated that soil could serve as a temporary reservoir for formaldehyde, i.e., a large fraction (~ 70%) of formaldehyde adsorbed by soil at high mixing ratios

could be re-emitted into the atmosphere at low ambient conditions, hence formaldehyde could cycle between the atmosphere and soil (Li et al., 2016). VOC emission from ground level can originate from the overlying soil litter (Gray et al., 2010;Warneke et al., 1999;Hayward et al., 2001;Schade and Goldstein, 2001), roots (Janson, 1993;Chen et al., 2004;Lin et al., 2007) and soil dwelling microorganisms (Scholler et al., 2002), for which the relative contributions depend on the soil type

5 and various environmental parameters such as ambient relative humidity (RH), soil water content, temperature (T), and VOC mixing ratio, etc.. Therefore, VOC formation from soils involves both biotic and abiotic mechanisms. The biotic processes include root exudation, degradation of soil organic matter and leaf litter by soil microorganisms. The abiotic mechanisms involve purely physicochemical reactions (e.g., heterogeneous and multiphase transformation, evaporation, desorption) and UV-light-enhanced emission from soil vegetation or decomposition of leaf litter (Riikka et al., 2002;Rinnan et al., 2003;Zepp

10 et al., 2007;Derendorp et al., 2011). The main mechanisms contributing to the uptake of VOCs were reported to include adsorption and degradation by roots (Simonich and Hites, 1995;Newman et al., 1997;Cho et al., 2005), biodegradation by microorganisms (van Roon et al., 2005) as well as physical/chemical adsorption by soil particles (Pignatello and Xing, 1996;Li et al., 2016).

15 Thus, both biotic and abiotic mechanisms can contribute to the exchange of VOCs on soils. Under real world conditions, the biotic and abiotic processes in soil are highly coupled and the net flux is the result of many complex multiphase interactions that are difficult to resolve. Furthermore, emissions from the soil may be uptaken or transformed in overlying leaf litter. Resolving the key processes requires the system to be examined in separate components. Here by applying a new reactor system we examine the physicochemical effects of soil on VOC exchange in isolation, but under real world conditions. From

20 the perspective of soil physicochemistry, VOCs can undergo reversible adsorption and irreversible surface reactions on soils and aerosol particles, coupling gas-surface transport (adsorption), surface-bulk transport (absorption/solvation), and chemical reactions in the bulk (Pöschl et al., 2007); and VOC oxidation/decomposition products can desorb immediately or further interfere with other reactants (Ammann and Pöschl, 2007). Heterogeneous processes at the gas–surface interface can be highly complex, and the individual steps controlling the reaction rates of heterogeneous processes are rarely known (Crowley et al.,

25 2010;Chapleski et al., 2016). Parameterizations of heterogeneous processes still tend to be empirical and most are untested in natural outdoor settings, where surfaces are prone to interferences of competitively co-adsorbing trace gas species and radicals, which is specifically crucial in the case of reactive trace gases like VOCs. While laboratory-based trace gas uptake studies normally apply individual VOC species separately, only little attention is given to interfering effects. However, laboratory studies on binary organic compound mixtures in the ppm level has shown that the photo-catalytic oxidation on catalytic

30 surfaces (TiO_2) of one VOC species may promote or inhibit the oxidation rate of another (Lichtin et al., 1996). In contrast to laboratory conditions, ambient air is a complex composite of a vast variety of gases, aerosols and radicals, and some components may exert synergistic effects on the heterogeneous chemistry of individual or categories of VOC species. Neglecting these synergistic effects may cause misleading results when extrapolating laboratory work to real world conditions.

This study aims to investigate the uptake, potential heterogeneous conversion and emission of VOCs on soil under real world ambient conditions. A flow tube system coated with pre-treated sterilized soil was used to investigate the physicochemical background of VOC exchange on soil independently from biological activity. Recently, the flow tube technique has been adopted to study the kinetics and mechanisms of reactive trace gas uptake onto soils (Wang et al., 2012;Donaldson et al.,

5   2014a;Donaldson et al., 2014b;VandenBoer et al., 2015;Li et al., 2016). These investigations, however, have focused on laboratory experiments under controlled environmental conditions, where the dependence on single relevant parameters was investigated while all others were kept constant. Here, the coated-wall flow tube system was deployed at an urban field site, which allowed ambient air to pass through the flow tube and the coated soil sample to interact directly with ambient VOC species. VOC uptake coefficients (γ), which indicate the fraction of trace gas kinetic collisions with a reactive surface that lead

10   to uptake by the surface (Ammann et al., 2013) are determined, and their dependencies on various environmental parameters are discussed. To the best of our knowledge, this is the first trial to deploy the flow tube technique for field observations to investigate uptake/emission kinetics of VOCs on soil under ambient conditions.

2 Methods

2.1 Soil sample preparation

15   Soil samples were collected from a scrubland site near Weiminghu lake in Peking University, Beijing, China (39°59´N, 116°18´E). Before collection, leaf litters were removed from the ground surface and only soil particles were obtained at a depth of 0-5 cm. The collected samples were air-dried in a shade place prior to grinding and sieving with a 120 mesh soil sieve. The soil pH was ~ 6.8 (1:2 soil/water (v/v), Thermo Scientific, OrionStar A211 pH meter). The soil texture comprised of 49% sand, 35% silt and 16% clay (wet sieving method) and the soil humus content was 8.8% (loss on ignition method) as analyzed by

20   Guangdong Institute of Eco-Environmental and Soil Sciences (Guangzhou, China). Since the purpose of this study was to investigate the physicochemical interactions between VOCs and soil, the sieved soil was autoclaved for 20 min at 394 K (repeated twice with an incubation time of one day) right before the flow tube coating procedure as in the work of Li et al. (2016). Autoclaving has been reported as the most effective sterilization method for eliminating soil microorganisms compared with other methods such as fumigation, UV and microwave irradiation (Razavi darbar and Lakzian, 2007). The sterilization

25   procedure and the autoclave time eliminated primary microbial impact on VOC exchange at the atmosphere-soil interface and minimized potential influence on soil physicochemical properties caused by the sterilization method itself (Berns et al., 2008). Moreover, a PTFE membrane filter installed upstream of the flow tube system could prevent the bacteria in the ambient air from inhabiting on the soil sample during the field measurement (see Sect. 2.2).

Soil slurry was prepared by mixing dry soil with sterilized deionized water (18.2 MΩ·cm, Millipore Corporation, Darmstadt,

30   Germany). The slurry was uniformly injected into a glass tube with sandblasted inner surface (100 mm length, 17 mm ID), which was then installed into an air-dried continuously rotating coating tool (ACRO). The design and performance of ACRO for soil coating had been described in the work of Li et al. (2016). The coated tube was rotated with a speed of 14 rpm and

flushed overnight with pure N_2 at a flow rate of ~ 0.5 L min^{-1} (purity ≥ 99.999%, RH = 0%). Note that the drying process with N_2, to some extent, purges VOCs off the soil sample. The coating mass has been shown to affect the gas uptake (Donaldson et al., 2014a;Li et al., 2016). A relatively large coating mass of ~ 95 mg cm^{-2} (corresponding to a geometric coating thickness ~ 500 μm) was chosen for our experiments. The coating procedure and mass has been experimentally shown to guarantee fair

5   homogeneity and reproducibility of the coating in our previous study (Li et al., 2016).

Prior to the VOC exchange experiment under ambient conditions, the freshly coated tube was flushed with N_2 (purity ≥ 99.999%, RH= 0%) for 40 min to scrub potential VOC impurities from the soil which were either adsorbed/absorbed onto the soil during the coating preparation procedure or from the soil coating itself. Note that during flushing with VOCs-free N_2,

10   many VOC species were indeed emitted (Fig. S.1). These emitted VOC species might originate from the soil surface and/or the soil bulk (including soil particles and residues of the autoclaved microorganisms) through pore diffusion. To quantify the soil layer depth contributing to these observed emissions, the desorption curves (in Fig. S.1) were fitted using the function derived in our previous study (the first function in Table 1 in Li et al., 2016) assuming that the emissions were a first order decay process. The determined desorption rate coefficient and desorption lifetime of the detected VOCs are listed in Table S.1.

15   The longest desorption lifetime is found for formaldehyde as ~ 22 min. Moreover, we estimated the time scale t for a VOC molecule diffusing through the entire soil coating thickness δ_g (~ 500 μm) using equation $t = \delta_g^2/D_a$, where D_a is the macroscopic diffusion coefficient of VOCs within soil pores. Adopting the lower limit of a macroscopic diffusion coefficient which typically range $10^{-4} - 10^{-2}$ cm^2 min^{-1} for clay minerals reported by Morrissey and Grismer (1999), a VOC diffusion time of ~ 25 min was obtained. This time scale is less than or comparable to our flushing time of 40 min, suggesting that the entire

20   soil layer could contribute to the VOC emissions by means of soil surface desorption/reaction and soil bulk pore diffusion. In addition, the amount of soil-emitted VOCs was estimated by integration of the desorption curve of methanol (which shows the highest emission signals, an order of magnitude higher than the others in Fig. S.1) using the fitting functions derived by Li et al. (2016). The emitted methanol mass is ~ 1.71 μg, which is far from being able to account for a monolayer coverage on the soil layer specific surface (see Sect. 2.3) when assuming an effective diameter of the methanol molecule of 4.2 Å according to

25   Perera et al. (2007). Thus, the flushing procedure could provide adsorption-sites devoid of reversibly absorbed VOCs on the soil surface as well as within the soil pores, and therefore allow focus on uptake kinetics from the initial phase (VOCs-free soil) of the exchange experiment.

2.2 Measurement site, experimental setup and operation

VOC exchange measurements were conducted within the campus of Tsinghua University, Beijing, China (40.00°N, 116.20°E),

30   from 25 August 2015 to 26 September 2015. This urban background site was 200 m east of a four-lane highway and 100 m west of a garbage station. There was a small mound nearby which was covered by grass land mixed with trees (mainly white poplars) on its northern side.

The aim of this study was to investigate VOC exchange at the atmosphere-soil interface under ambient conditions, where air temperature (T), relative humidity (RH) and VOC mixing ratio, etc. all change in concert. A flow tube system was installed in a self-built sampling box, which was located on the roof of a 2.35 m high storage container. Two openings on the sampling box allowed for direct access of ambient air into the flow tube system. The sampling box was covered with a thin non-transparent PTFE film (coated with an aluminium foil and with a total thickness of ~ 0.5 mm) that functioned as both a reflector for sunlight and a shelter from rainwater. The flow tube system consisted of a sample channel and a reference channel. The sample channel was equipped with a soil-coated tube in front of which a pre-tube or entrance region (with the same dimensions as the soil-coated tube, i.e., 100 mm length, 17 mm ID, but without soil coating) was installed to ensure well-developed laminar flow in the soil-coated part (Li et al., 2018). The reference channel used a ¼ inch (i.e., 6.35 mm O.D.) PFA Teflon tube (200 mm length) without coated soil. As shown in Fig. 1, ambient air was introduced into the flow tube system prior to being analyzed by a proton-transfer-reaction mass spectrometer (PTR-MS). By using solenoid valves, VOCs from the sample and reference channels were alternately analyzed by the PTR-MS (with 60 min for each channel). While one channel was connected with the PTR-MS, the other was simultaneously flushed by ambient air with the same flow rate as of the PTR-MS (~ 0.1 L/min) to prevent potential accumulation/depletion of VOCs under otherwise static conditions. PTR-MS analysis was paused on the 4 - 8th of September 2015, but the flow tube was continuously flushed with ambient air to ensure uninterrupted exposure of the soil sample to dynamic ambient conditions.

When the reference channel was connected to the PTR-MS, the detected VOC signals represented their mixing ratios in ambient air (VOC depletion within the PFA Teflon tube was negligible), denoted as C_r, which was also equal to the VOC mixing ratios at the sample tube inlet. When the sample channel was connected, the detected signals represented the VOC mixing ratios subject to interactions with the coated soil, designated as C_s. Considering the short residence time (~ 24 s) within the sample tube volume, gas-phase-reactions-induced depletion of VOCs only accounted for a small faction (~ 3% for very reactive species like isoprene and much less for the others, estimated based on the measured gas oxidants mixing ratios (see Sect. 3.1) and assuming a background mixing ratio level of 1 ppt for OH radicals). Thus, the VOC mixing ratio difference between the reference channel and the sample channel, $C_r - C_s$, can be assumed to be mainly due to exchange of VOCs on soil. Note that the PTR-MS couldn't detect C_r and C_s simultaneously, when one channel was connected to the PTR-MS the corresponding VOC mixing ratios of the other were determined afterwards by interpolating the adjacent measured values. Before the start of field measurements, a PTFE membrane filter (Φ: 50 mm, pore size: 0.2 µm, Millipore Corporation, USA) was installed at the air inlet of the VOC exchange system to filter bacteria as well as other particles in the ambient air. Filters were replaced every three or four days.

A commercial high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria), located in the aforementioned container, was used for the detection of a broad range of VOCs including isoprene, oxygenated VOCs, acetonitrile, and C6 – C7 aromatics with a time resolution of ~ 30 s (Table 1). PTR-MS is an analytical mass spectrometry technique that uses gas phase hydronium

ions (H_3O^+) as ion source reagents (Lindinger et al., 1998;Yuan et al., 2017). Inside the PTR-MS drift tube, VOC species with greater proton affinity than that of water are soft-ionized by reactions with H_3O^+ and then detected by a quadruple mass spectrometer (Lindinger et al., 1998). This PTR-MS has been validated and utilized in previous field campaigns (Yuan et al., 2012;Chen et al., 2014;Yuan et al., 2013). During the field measurement, the system was running in multiple ion mode, where the quadruple switched between the selected masses. Most of the masses were recorded for 1 s in every cycle, except for m/z 21 (0.2 s). Background signals were measured for 30 minutes every 4 hours by diverting the ambient air into a platinum catalytic converter at 370 °C (Shimadzu Inc., Japan). Aromatics, oxygenated VOCs, isoprene and acetonitrile were calibrated by a pressurized gas standard (Spectra Gases Inc., USA). Formaldehyde (m/z = 31), formic acid (m/z = 47) and acetic acid (m/z = 61) were calibrated by permeation tubes (VICI Inc., USA). Calibrations were conducted before and after the measurement period, and a single-spot calibration was conducted every three or four days with response factors varying within 15%. Uncertainties of measured species were about 5% - 15%, with the notable exception of formaldehyde, formic acid and acetic acid. Limits of detection (LOD) for the measured species were in the sub-ppb level listed in Table 1.

Formaldehyde detection is found to be significantly influenced by RH (Vlasenko et al., 2010;Warneke et al., 2011;Baasandorj et al., 2015). Calibrations were conducted within a range of RH (0 - 30 mmol/mol) to fit the response curve, which was then applied in ambient measurement calculations and this procedure resulted in a measurement uncertainty within ± 20%. Measurements of formic acid by PTR-MS can potentially suffer interference from ethanol and dimethyl ether when they are present in significantly higher abundance than formic acid (Baasandorj et al., 2015). At the background urban site, however, the atmospheric abundance of ethanol and dimethyl ether in similar urban site has previously been found to be low (Good et al., 1998;Monod et al., 2003;Jia et al., 2012), giving rise to a measurement uncertainty within ± 30%. Influences from ethyl acetate on acetic acid have been found in field campaigns (Fortner et al., 2009;Baasandorj et al., 2015;Derstroff et al., 2017). Therefore, during calculations of acetic acid concentration the m/z = 89 (attributed to ethyl acetate) was introduced to correct for the influences (Yuan et al., 2013). However, this introduced a measurement uncertainty up to > 40 %.

In addition to measurements of VOC species by the PTR-MS, several common air pollutants were also monitored by Thermo Scientific analyzers: O_3 (Model 49*i*, UV photometric O_3 analyzer), CO (Model 48*i*, trace-level-enhanced gas filter correlation CO analyzer), NO_x (Model 42*i*, trace level chemiluminescence NO-NO_2-NO_x analyzer) and SO_2 (Model 43*i*, trace-level-enhanced pulsed fluorescence SO_2 analyzer). These analyzers were calibrated every three days and uncertainties of these measured air pollutants were less than 5%.

2.3 Uptake coefficient and deposition velocity

The uptake coefficients (γ) of measured VOC species under ambient conditions were determined using a Cooney-Kim-Davis (CKD) method (CKD-B in Li et al., 2016). This CKD-B method is based on the commonly used CKD solution for correction of radial diffusion effect (Murphy and Fahey, 1987), and has been shown to have a much better accuracy than CKD

interpolation method, as CKD-B directly solves a governing differential equation with numerical methods. The CKD-B can establish the relation between the sample tube penetration (i.e., C_s/C_r) and γ of the measured VOC species, which is shown in Fig. 2 derived at an average ambient temperature of 25 °C as an example. For details of the CKD-B method, see our previous study (Li et al., 2016). Note that the uncertainty of the determined γ depends on the uncertainty of C_s/C_r as well as the relation

5   between C_s/C_r and γ (as in Fig.2), here with the derived γ range of 10^{-7}- 10^{-6} (see Sect 3.3 and 3.4) the estimated uncertainty of γ for each VOC species was within one order of magnitude. The Reynolds number (*Re*) in our experiment was ~10, which ensured laminar flow conditions requiring $Re <$ ~2000 (Murphy and Fahey, 1987;Knopf et al., 2015;Li et al., 2018). The pre-tube/entrance region length was 10 cm, and full development of laminar flow was achieved within the first ~ 1 cm for our setup. When a geometric coating thickness δ_g is larger than a critical height δ_c, the coating surface roughness may potentially

10   distort the well-developed laminar flow and introduce uncertainties in the calculated uptake coefficients corrected for molecular diffusion effects using conventional diffusion correction methods (Li et al., 2018). According to this δ_c criterion, the geometric coating thickness of our soil sample (~ 500 μm) was much smaller than the calculated δ_c (~ 2400 μm) based on our experimental configuration, ensuring that the soil coating surface roughness effect was negligible. The uptake coefficients reported here are based on the geometric surface area of the soil sample, considering that in atmospheric models soil

15   microstructure is likewise not taken into account (Donaldson et al., 2014a). The specific surface area of the soil, however, was also measured using a water vapor adsorption method based on the Brunauer-Emmett-Teller (BET) adsorption theory (Brunauer et al., 1938) being 15 ± 1.5 m^2 g^{-1}. To calculate the BET surface area, the mass of the adsorbed water on soil sample after equilibrium with pre-defined RH levels was determined by a non-dispersive infrared (NDIR) gas analyzer (type: Li-6262, LI-COR Biosciences Inc.) operated in differential mode. This BET surface area is comparable to that in other reports on similar

20   soil types, e.g., 12-15 m^2 g^{-1} (Kahle et al., 2002) and 8 - 19 m^2 g^{-1} (Punrattanasin and Sariem, 2015). Accounting for the BET results, the specific surface area would reduce γ by a factor of 10^4 in our case.

The primary controlling factors of VOC exchange at the soil-atmosphere interface include gas transport and the concentration gradient between the soil surface and the atmosphere. As depicted in Fig. 3, the transport of a gas species to soil surfaces is

25   governed by three resistances in series: the aerodynamic resistance R_a, the quasi-laminar layer resistance R_b, and the soil surface resistance R_c (Seinfeld and Pandis, 2016). The deposition or transfer velocity V_d is the inverse of the sum of these three resistances (Seinfeld and Pandis, 2016). With the coated-wall flow tube technique employed in this study, the derived γ reflects the reaction kinetics on soil and thus relates to R_c rather than R_a and R_b. Based on the calculated γ, R_c can be further derived according to equation $R_c = 4/(\omega \times \gamma)$ (Donaldson et al., 2014b;Dentener et al., 1996), where ω denotes the mean molecular speed

30   of the VOC species. Approximations of R_a and R_b can be achieved using the methodology developed by Seinfeld and Pandis (2016), i.e., R_a and R_b can be derived based on Eqs. (1) and (2), respectively.

$$R_a = \frac{1}{\kappa u_*} ln(\frac{z}{z_0}) \tag{1}$$

$$R_b = \frac{5 \, Sc^{2/3}}{u_*} \tag{2}$$

where κ is the von Karman constant, u_* is the friction velocity, z is the height above the ground, z_0 is the roughness length and Sc is the dimensionless Schmidt number.

For the basic assumptions and utilized parameters during derivations of R_a and R_b, see Sect. 3.2. Finally, v_d can be estimated as $V_d = 1/(R_a + R_b + R_c)$.

3 Results and discussion

3.1 Site specific characteristics of selected air quality indicators

Figure 4 shows the time series of site specific ambient air pollutant mixing ratios observed during the whole measurement period (A) and respective mean diel courses (B). The range of mixing ratios of selected air quality indicators like ozone (O_3), carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are representative of polluted urban conditions (Bigi and Harrison, 2010). O_3 reveals peak mixing ratios in the afternoon (13:00 – 17:00 local time), which corresponds to high sunlight intensities and temperatures at this time of the day. Coincident with this maximum in O_3, reactive nitrogen species (NO_2 and NO) show decreasing trends, which may be due to decreased local NO_x emissions, and/or rapid photochemical oxidation or strong dilution in the boundary layer in the afternoon. Even though most of the selected air quality indicators reveal a significant diel cycle, CO, NO and NO_2 do not show a typical urban rush-hour pattern with traffic-associated peaks during morning and late afternoon. Rather, the site represents an urban background site without direct influences of strong nearby point sources. The relatively weak diel course of SO_2 mixing ratios with maxima during daytime can also be assumed to stem from long-range advection or midday entrainment of high concentration air masses from aloft, instead of nearby presence of ground-level emission sources (Bigi and Harrison, 2010).

3.2 Site specific characteristics and exchange of VOCs

Figure 5 displays the time series of site specific ambient air mixing ratios of VOCs, temperature (T), relative humidity (RH) during the whole measurement period (A), and respective mean diel courses (B). Among the measured VOC species, methanol has the highest mixing ratios (Fig. 5A). Methanol is ubiquitous in the lower atmosphere with mixing ratios in remote regions reported to be ~ 1 ppb (Galbally and Kirstine, 2002;Jordan et al., 2009). The high mean daytime mixing ratios of 10 - 20 ppb at this urban background site suggest strong impact of anthropogenic emissions on the local methanol budget. High mixing ratios are also found for its oxidation products formaldehyde (~ 10 ppb) and formic acid (~ 5 ppb), respectively. Formaldehyde is a key reaction intermediate of the atmospheric oxidation cycle (Li et al., 2016), and hence an indicator of the total amount of OVOCs. Its increasing trend during daytime (Fig. 5B) is indicative of strong photochemical formation. In contrast, formic acid, which can be formed from ozonization of all terminal double-bonded molecules (Osamu et al., 1994), shows lower mixing

ratios during daytime than during nighttime, and similar diel trends are also found for other species including toluene, methanol, acetonitrile and benzene. The daytime decrease of the latter may be due to dilution effects by increased daytime boundary layer mixing height and/or lower atmospheric photochemical formation rates during daytime, even though some of them (e.g., formic acid) have smaller photolysis and oxidation loss rates than those of formaldehyde. On the other hand, the most significant diel profile is observed for isoprene, with mixing ratios peaking at midafternoon (around 15:00, local time) followed by a decline at late afternoon stabilizing at ~ 0.5 ppb during night. Isoprene can have an important impact on the atmospheric oxidation capacity due to its high OH reactivity both in pristine and in polluted urban regions (Williams et al., 2016). Besides anthropogenic sources like gasoline and diesel traffic exhaust (Borbon et al., 2001;Wang et al., 2013;Wagner and Kuttler, 2014), the major summertime source of isoprene can be assumed to be biogenic, i.e., being emitted from vegetation in a light and temperature dependent manner (Guenther et al., 1993). Thus, during daytime, high mixing ratios of biogenic isoprene are anticipated at our measurement site, which was surrounded by different types of vegetation cover (see Sect. 2.2). Following the diel trend of isoprene, the two primary photochemical oxidation products of isoprene, methyl vinyl ketone (MVK) and methacrolein (MACR), also exhibit higher mixing ratios during daytime than during night.

Besides primary or secondary surface sources and sinks, the near-ground nighttime increase (or decrease) of atmospheric trace gas mixing ratios is favored by the development of a stable and shallow nocturnal boundary layer (NBL). Any nighttime emission (or deposition) of trace constituents is confined to the relatively small volume of the NBL where they accumulate (or get depleted). The growth of the atmospheric boundary layer (ABL) in the morning hours due to the influx of sensible and latent heat, and resulting upcoming convection, and the respective re-entrainment of air from the residual boundary layer aloft, being enriched with (or depleted of) atmospheric trace constituents, may confer a reasonable explanation for any increased (or reduced) daytime mixing ratios (Kuhn et al., 2002).

The exchange properties of VOCs on soil can be reflected by comparing C_r (colorful lines in Fig. 5A) and C_s (black lines in Fig. 5 A). The confidence bands (best estimate ± measurement uncertainties) of C_r and C_s for each species can be found in Fig. S.2. As shown in Fig. 5A, during the whole measurement period most of the VOC species are taken up by the soil, especially for styrene, formaldehyde, toluene and acetic acid, indicated by the discernable differences between their C_r and C_s. Only formic acid shows a slightly higher C_s than C_r, suggesting this compound is likely emitted by the soil. The time series of the mixing ratio difference $C_r - C_s$ of measured VOCs are further displayed in Fig. S.3. The integrated total amount and average surface flux of each absorbed or emitted VOC species on soil for the whole measurement period is listed in Table S.1.

3.3 Time series and mean diel courses of VOC exchange

Based on the measured C_r and C_s, the uptake coefficients of examined VOC species can be derived (see Sect. 2.3). To minimize potential impacts of measurement uncertainties (e.g., random noise of the instrument) on small $C_r - C_s$ (or large C_s/C_r) and further on the derived uptake coefficients, the calculated hourly based uptake coefficients (basing on the measured hourly

mixing ratio data) were averaged to a daily basis (i.e., daily mean uptake coefficients). Figure 6A shows the time series of daily mean VOC uptake coefficients, together with those of ambient temperature (T) and relative humidity (RH). Eight species (i.e., styrene, toluene, isoprene, MVK+MACR, acetaldehyde, MEK, acetone and acetonitrile) exhibit a relatively high initial uptake coefficient, followed by a significant decrease in the first few days, indicative of progressive saturation of absorption sites on the pre-treated soil sample. For styrene and acetonitrile, this decrease prevails for the whole one-month measurement period. Occasionally, some species show short-term swaps between deposition and emission (see Fig. S.4 for the complete time series of hourly averaged data). This bidirectional exchange can be caused by fast dynamics in ambient air conditions like temperature, relative humidity and trace gas mixing ratio, and respective status of soil saturation. Interestingly, formaldehyde only rarely shows emission from soil, suggesting strong capacity of the soil sample for absorption under ambient conditions. This result to some extent challenges our previous laboratory-based observation that soil could also act as a source for formaldehyde, when it had been saturated with formaldehyde prior to back-flushing with pure N_2, i.e., the uptake of formaldehyde by soil was shown to be reversible (Li et al., 2016). Indeed, the range of formaldehyde mixing ratios observed in Beijing was rather high for most of the time, and extremely rapid changes of mixing ratio to below a compensation point, as applied in the laboratory study, hardly occurred in the field. On the other hand, the anticipated high levels of oxidants for heterogeneous reactions on the soil under field conditions may foster the chemical conversion/oxidation of formaldehyde, that could prevent its accumulation, saturation and subsequent release (see below). Given the poor understanding of formaldehyde's budget (Jacob, 2000;Wagner et al., 2002), more research is needed to elucidate the exchange behavior of formaldehyde on various types of soils under ambient conditions. In addition, the variability of uptake coefficients of some species (e.g., isoprene, MVK+MACR, acetaldehyde, and formic acid) closely follow the trend of ambient relative humidity and temperature, suggesting that these environmental parameters influence the exchange of respective VOC species.

Mean diel variations of VOC uptake coefficients as well as those of ambient relative humidity (RH) and temperature (T) are presented in Fig. 6B. In general, uptake coefficients are quite stable over the whole day.

The observed uptake/emission in Fig. 6 can be caused by pore diffusion and soil surface processes (i.e., adsorption/desorption equilibrium and chemical reactions). As aforementioned, the time scale of VOC diffusion through soil pores is around 25 min. This time scale is several orders less than our whole field campaign time period (i.e., 1 month), suggesting that pore diffusion is not the limiting factor of the uptake/emission found here. After the significant absorption saturation on soil in the first few days (see Fig. 6A), the subsequent relatively stable uptake for most of the VOC species can be due to chemical reactions on soil surfaces. Our previous laboratory study of formaldehyde uptake on soil has proved that the observed uptake is a combination of adsorption/desorption equilibrium and chemical reactions (Li et al., 2016). From a perspective of kinetic gas theory, the derived uptake coefficients can be further used to determine VOC surface reaction rates on soil which are only caused by reactions on soil surface instead of diffusion into soil pores under steady state conditions (i.e., after significant absorption saturation of the soil sample in the first few measurement days in Fig. 6A). The soil surface reaction rate is described

as: $(\gamma \times \omega)/4 \times$ [VOC(g)]. γ and ω are the daily average uptake coefficients and mean molecular speed (at an average temperature of 298 K) of each VOC species, respectively. [VOC(g)] is the VOC mixing ratio in ambient air (i.e., C_r). Accordingly, the corresponding surface reaction (or wall loss) rate coefficient k_w is $(\gamma \times \omega)/4$, equivalent to the inverse of R_c. Note that only formic acid shows negative uptake coefficients for most of the measurement time period, and its emission rate cannot be described by the above reaction rate expression accounting for surface uptake processes. Instead, the soil surface emission rate of formic acid is calculated from a flux point of view, which equates to $F \times (C_r - C_s)/S$. F is the volumetric flow rate in the sample tube and S is the geometric surface area of the soil sample. The time series of surface reaction rates are shown in Fig. S.5. k_w is shown in Table S.3 and further discussed in the following section.

3.4 Exchange of VOCs interpreted in terms of long-term mean uptake coefficients and deposition velocities

Figure 7 shows the averaged uptake coefficients for days with continuous instrumental operation (16 days within the one-month field measurement) for each VOC species. The vast majority of VOC species reveal positive uptake coefficients, indicating that these species tend to be absorbed and retained or converted into other products in the soil (net soil influx). Highest uptake coefficients are found for styrene and formaldehyde, with mean values in the order of 10^{-6}. The uptake coefficient of formaldehyde is in the same range as reported earlier for laboratory experiments, where sterilized agricultural soil was flushed by pure N_2 containing different mixing ratio levels of formaldehyde under varying RH conditions (Li et al., 2016).

In Fig. 7, only formic acid reveals a negative mean uptake coefficient, which is indicative of emissions from soil (Li et al., 2018). This short-chain organic acid is regarded as one of the terminal products in the oxidation processes of many VOC species present in the atmosphere (Charbouillot et al., 2012). Therefore, the heterogeneous formation from previously adsorbed/absorbed VOCs may confer a reasonable explanation for its accumulation and subsequent release, as further discussed in following sections.

As mentioned previously, the long-term mean uptake coefficients can be used to derive the soil surface reaction (or wall loss) rate coefficient k_w of each VOC species, which reflects the soil surface exchange properties. Here k_w has a unit of cm s^{-1} and can be interpreted as a deposition velocity without gas transport resistance (i.e., $R_a + R_b$) effects (Pöschl et al., 1998). As the initial soil sterilization procedure eliminates potential impacts from soil bacteria, the observed exchange of these VOC species is primarily influenced by physicochemical factors. To have a general understanding of how different physicochemical factors may affect k_w, the calculated k_w of each VOC species are listed in Table S.3, together with the basic physicochemical parameters possibly related to the trace gas exchange (i.e., gas phase reaction rate coefficients with OH radicals and O_3, Henry's law constant, vapor pressure and octanol-water partition coefficient). In general, differences of k_w found among these species cannot be explained by any of the physicochemical factors alone, which suggests that VOC exchange at the atmosphere-soil interface is a complex multifunctional process.

Deposition velocity V_d is a key parameter used in models to describe trace gas uptake by soils and is the inverse of the sum of three resistances in series: the aerodynamic resistance R_a, the quasi-laminar layer resistance R_b, and the soil surface resistance R_c (Fig. 3). As described in Sect. 2.4, only R_c can directly be derived from the calculated uptake coefficients. R_a and R_b are

5   calculated adopting the approach proposed by Seinfeld and Pandis (2016): In Table 2, the case of neutral stable temperature profiles is adopted for R_a calculation (Eq. 19.14 in Seinfeld and Pandis 2016). The season is set to autumn (cropland before harvest). To assess the impact of R_a and R_b on derived V_d, three types of land use categories including shrubs (category 1 in Table 2), urban (category 2) and barren land (category 3) are selected mimicking our field environmental conditions and soil type characteristics. The detailed parameters adopted for R_a and R_b derivation and the calculated R_a, R_b, R_c and V_d are shown

10   in Table 2. As $R_c >> R_a + R_b$, the VOC uptake is not limited by atmospheric gas phase transport (R_a+R_b) or by land use type. Rather the uptake on the soil surface (R_c) is the primary rate-limiting step for dry deposition of these VOC species, even for the largest γ observed in our study. Note that V_d of formic acid intrinsically reveals negative values, as this organic acid is released from the soil.

15   Previous VOC exchange studies on various soil types such as agricultural soil, tropical soil, plantation floor and forest understory, etc., have spanned a huge range of V_d with three orders of magnitude (0.01 – 1 cm s^{-1}) for the VOC species investigated here (Hartmann et al., 1991;Karl et al., 2005;Sanhueza et al., 2004;Schade and Custer, 2004;Stickler et al., 2007;Jordan et al., 2009;Schade et al., 2011;Gordon et al., 2014b;Cleveland and Yavitt, 1997). Our calculated V_d (0.001 – 0.01 cm s^{-1}) is at the very low end of previous studies. This can be due to a variety of reasons: (1) our soil sample is bare soil without any vegetation cover while previous flux studies included different types of vegetation covers (grass, leaf litter, agricultural

20   crops, etc.), which might significantly alter the measured deposition velocity; (2) our soil sample is sterilized aiming to investigate the physiochemical processes on soil, yet the soil bacteria can significantly modify the VOC exchange as can be expected in the previous studies. In fact, several studies have demonstrated that soil bacteria can consume atmospheric VOCs (Misra et al., 1996;Cleveland and Yavitt, 1998;Stacheter et al., 2013;Lynch et al., 2014). From the physicochemical point of

25   view, low V_d may also arise from competitions among different VOC species for surface absorption sites, as has been observed in controlled laboratory studies by Lichtin et al. (1996) for photo-catalytic reactions of binary VOC mixtures on TiO_2 surfaces. Likewise, interfering effects of O_3, OH and NO_3 radicals on VOC photo-catalytic TiO_2 surface reactions could be demonstrated (Ao et al., 2004). We assume that this phenomenon is universal for catalytic surfaces and also applies for soil.

30   To further validate the plausibility of our calculated γ and derived V_d, we calculate the surface resistance, R_c, using a regional-scale numerical model developed by Wesely (Seinfeld and Pandis, 2016;Wesely, 1989), which considered only physicochemical factors affecting gas deposition on ground surface for formaldehyde, acetic acid and acetaldehyde as typical VOC representatives. As a proxy for bare soil properties in the present study, the land use type is set to barren land (mostly desert), and the seasonal category is chosen as autumn (cropland before harvest). All other input parameters are the same as

used in the original literature (Wesely, 1989). The model outputs a R_c for formaldehyde of 167 s cm^{-1}, which is in fair agreement with our results (98 s cm^{-1}). Due to a very small effective Henry's law constant adopted in the model (15 M atm^{-1} for water with near-neutral pH) the derived R_c for acetaldehyde is even much higher than based on our measurements (66667 s cm^{-1} versus 291 s cm^{-1}), corroborating our relatively low range of observed VOC uptake. In contrast, acetic acid bears a much higher

5 effective Henry's law constant (4×10^6 M atm^{-1}), revealing a much smaller R_c than based on our measurements (0.3 versus 214 s cm^{-1}), underpinning the intense impact of VOC physicochemical characteristics on modelled uptake resistances.

3.5 VOC exchange dependence on environmental parameters

In order to explore potential effects of environmental factors on the exchange of these VOC species at the atmosphere-soil interface, the relation between uptake coefficients and ambient relative humidity (RH), temperature (T) and mixing ratio (C)

10 is further examined, and those VOC species showing relatively significant dependencies are shown in Fig 8. To interpret the uptake coefficient dependence on a single parameter, the others should remain constant. Under ambient conditions, however, all the environmental parameters change simultaneously and some of them are even closely related (e.g., between RH and T, see Fig. 5). Therefore in Fig. 8 we present the RH/T dependence as the C varies within a narrow range (i.e., this range can be considered constant when compared with the whole variation scope of C during the entire measurement time period). The C

15 range for the species in Fig. 8 is: 0.5-0.6 for isoprene, 0.8-1.0 for MVK+MACR, 2.0-6.0 for formic acid, 8.0-12.0 for formaldehyde and 1.5-2.5 for acetaldehyde. These ranges are determined following the criterion of A ± B, where A means the one-month-average of the ambient mixing ratios of each species and B is determined by using two criteria: (1) it should be as small as possible; (2) the selected range can provide a data set large enough for plotting the RH/T dependence box chart. Regarding the C dependence in Fig. 8, only the data is adopted when RH equals to 50%.

RH affects the amount of surface-adsorbed water and can accelerate or slow down trace gas uptake rates (Crowley et al., 2010). High-RH induced condensed water may attract water-soluble or hydrophilic gas species and hence enhance their uptake (Pei and Zhang, 2011), or decrease their net emission. This mechanism applies, e.g., to hydrophilic formaldehyde and formic acid (see Table S.3 for respective Henry's law constants). On the other hand, more water molecules on soil surfaces tend to repel

25 the hydrophobic species more strongly or reduce gas uptake by means of competitive adsorption effects between water molecules and gas species (Ruiz et al., 1998;Goss et al., 2004;Donaldson et al., 2014a;Li et al., 2016). However, the uptake coefficients of hydrophobic isoprene and its primary degradation products (i.e., MVK+MACR) also increase at high RH. This counterintuitive dependence may also be explained in another way: more water molecules can push more hydrophobic species into the soil bulk, leaving additional adsorption sites on soil surfaces and thereby increasing its uptake; As the soil becomes

30 dry, the VOC molecules in the soil bulk will remain in situ considering that the timescales of soil bulk diffusion are considerably longer than on soil surfaces. From the physical perspective of vapor pressure, increased temperature leads to decreased trace gas uptake and increased emission. This is in line with the decreased uptake of isoprene at higher temperatures shown in Fig. 8. However, the uptake coefficients of acetaldehyde show a slight increasing trend as a function of T.

Even though the calculation of uptake coefficients intrinsically accounts for the gas phase mixing ratios, higher mixing ratios have been shown to reduce uptake coefficients (Sassine et al., 2010;Wang et al., 2012). A negative effect of increased mixing ratios on uptake coefficients is also observed for isoprene and acetaldehyde in Fig. 8. The negative effect of mixing ratios on

5   uptake coefficients can be understood as competition among the individual VOC molecules for reactive uptake sites, or with other VOCs whose mixing ratios show a simultaneous increase (Li et al., 2016). Our previous laboratory experiments on formaldehyde (Li et al., 2016) showed that this trend was more pronounced under dry conditions (RH = 0%) than under humid conditions (RH = 40%), in agreement with the formaldehyde pattern shown here.

3.6 VOC exchange correlation analysis

10   As discussed above, the uptake dynamics of one individual VOC species may be biased, either (i) by competitive co-absorption of other VOCs or trace gases from ambient air (Lichtin et al., 1996;Ao et al., 2004), or (ii) by formation on the soil through heterogeneous conversion of precursor compounds that have been absorbed earlier (Ammann and Pöschl, 2007;Pöschl et al., 2007), or (iii) by depletion of the individual VOC species due to heterogeneous degradation. To explore potential interactions/interferences of VOC species among each other, correlation analyses of the exchange rates (i.e., the concentration

15   difference between the reference channel and the sample channel $C_r - C_s$ times the volumetric flow rate F) of measured VOC species are conducted for each pair of species. The results are presented in Fig. 9 in terms of Pearson correlation coefficients, together with the molecular structure of each investigated species. The interplay of sorption, heterogeneous reactions and desorption kinetics of VOCs is complex, and heterogeneous reactions may require time periods from milliseconds to weeks or even months to reach equilibrium (Xing and Pignatello, 1996;Ammann and Pöschl, 2007). Hence, to also account for slow

20   kinetics, the correlation analysis in Fig. 9 is based on daily integrals. VOC exchange rates instead of uptake coefficients are used to allow for a budget approach. Positive correlations are indicated in red colors, and some pairs of VOC species show high positive correlation (deep red color code in Fig. 9), suggesting they have similar exchange characteristics. For example, MVK and MACR are the first generation oxidation products of isoprene (Jordan et al., 2009). Thus, the observed high correlation coefficient between MVK+MACR and isoprene can be explained by their similar molecular structures shown in

25   Fig. 9. The same holds for the strong correlation between methanol and formaldehyde, methanol and acetone, as well as for MEK and acetone: similar molecular structures and functional groups result in analogous exchange and reaction mechanisms on soil.

Negative correlations in Fig. 9 are indicated in blue colors. As aforementioned, formic acid is at the very end of the VOC

30   oxidation chain, and is exclusively emitted from the soil sample while all other VOCs tend to be taken up. Thus, correlations of formic acid with other VOCs are negative as such (blue in Fig. 9). High negative correlation coefficients are obtained between formic acid and some species (i.e., acetone, isoprene, formaldehyde, styrene and methanol), indicative of possible generation and emission of formic acid due to heterogeneous transformation of these deposited compounds.

4. Implications for atmospheric chemistry

4.1 Formic acid formation through heterogeneous transformation of deposited VOCs

We know from the above discussions that several VOC species including acetone, isoprene, formaldehyde, styrene and methanol show high anti-correlation with formic acid, suggesting the existence of one or several pathways for formic acid
5   formation through heterogeneous reactions of these VOC precursors.

In the atmosphere, photo-oxidation of acetone contributes to the abundance of formic acid, and the dominant pathway for formic acid formation via acetone photo-oxidation is the reaction of OH radical with acetone-derived formaldehyde (Chattopadhyay et al., 2015). Formic acid production through photo-oxidation of isoprene has been found under high NO_x
10   circumstances (Paulot et al., 2009). Under ambient conditions, gas phase reactions of styrene with OH radical and O_3 can occur respectively, with formaldehyde and benzaldehyde as major products and formic acid as the minor (Tuazon et al., 1993). Methanol has been reported to play an important role in upper tropospheric photo-oxidation chemistry via its contribution to the HO_x budget after its oxidation to formaldehyde (Tie et al., 2003;Singh et al., 1995;Singh et al., 2000;Singh et al., 2004;Colomb et al., 2006). Notably, formaldehyde is an important intermediate of VOC oxidation and a direct precursor of
15   formic acid (Adewuyi et al., 1984;Chameides, 1984). Moreover, the results in Sect. 3.2 and 3.3 tell us that formaldehyde shows continuous and even increasing uptake during the whole field measurement (see Fig. 5A and 6A). All these results suggest formaldehyde may act as the best candidate for heterogeneous formation of formic acid on soil.

In terms of physicochemistry, formaldehyde is much less stable than formic acid (~ 1 day versus ~ 25 days of mean atmospheric
20   chemical lifetime, see Millet et al., 2015), indicating its faster turnover rates on soil surfaces. Moreover, the mean retention coefficient of formaldehyde has been shown to be considerably higher than for formic acid in cloud/ice water (Jost et al., 2017), inferring a reasonable explanation for the preferential release of the organic acid from the soil. Furthermore, aldehydes in general undergo accretion reactions (i.e., aldol condensation type reactions) in acidic media and similar chemistry has been shown to occur on mineral oxides (Li et al., 2001), therefore mineral-rich bare soils can serve as a sink for these compounds.
25   According to our results, formaldehyde is a relatively reactive short-term intermediate for formic acid production, rather than being directly released to the atmosphere under authentic ambient air oxidizing conditions in Beijing city. In general, a catalytic effect of soil can be anticipated by its composition of a variety of mineral oxides (silicon oxide, iron oxide and titanium oxide, etc.). Therefore, our soil sample may serve as a catalytic surface for degradation of the deposited precursors with formaldehyde as the most important intermediate, which can be further oxidized to build up formic acid by heterogeneous reactions on the
30   soil, followed by formic acid emission. This catalytic effect may be further enhanced by the co-existence of other deposited oxidants (O_3, OH radical, NO_2 and peroxides, etc.) on the soil surfaces. More research is needed to confirm the speculation made here.

4.2 Physicochemical reactions on bare soil and soil-derived dust may act as a potential source of formic acid

The only VOC that have been observed to be released from the soil sample investigated here is formic aid, which represents a final organic product of the VOC oxidation cascade. Formic acid is one of the most abundant organic acids in the atmosphere, existing in gas phase, cloud and rain water as well as snow and even polar ice (Chebbi and Carlier, 1996;Sanhueza and Andreae, 1991;Maupetit and Delmas, 1994;Sempére and Kawamura, 1994;Löflund et al., 2002;van Pinxteren et al., 2005;Mungall et al., 2018). In remote regions like the Amazon forest, short-chain organic acids have been shown to be responsible for 60 - 80% of rainwater acidity (Galloway et al., 1982;Stavrakou et al., 2012), and also over boreal forests and in urban areas they contribute significantly to the free acidity in precipitation (Khare et al., 1999;Stavrakou et al., 2012), and hence can regulate pH-dependence of aqueous reactions in clouds (Vet et al., 2014) and can contribute to acidification of soil.

Gas phase photochemical oxidation of biogenic VOCs is considered to be the dominant global atmospheric source of formic acid. Modelled budget analyses implicate the existence of one or more large missing sources for formic acid, i.e., the annually produced formic acid (100 - 120 Tg yr^{-1}) is two to three times that can be explained based on the current understanding of primary and secondary (gas phase) atmospheric processes and aqueous-phase cloud/rain chemistry (Barth et al., 2007;Paulot et al., 2011;Veres et al., 2011;Le Breton et al., 2012;Stavrakou et al., 2012;Cady-Pereira et al., 2014;Schobesberger et al., 2016;Millet et al., 2015), even when using a Master Chemical Mechanism (MCM) that was updated with recently proposed additional photochemical formation pathways for formic acid, like OH oxidation of isoprene and aromatics (Yuan et al., 2015). This suggests the existence of either a key gap in current understanding of hydrocarbon oxidation or large and widespread, yet unidentified sources for formic acid (Millet et al., 2015).

Previous model estimations of soil emissions of formic acid were based on a few available field measurements (Paulot et al., 2011;Millet et al., 2015). These ambient studies found formic acid emissions from dry savanna soil (Sanhueza and Andreae, 1991) and coniferous forest soil (Enders et al., 1992), respectively, to be an important source of the local formic acid budget. The former study reported daily average emission rate of 1.4×10^{-1} nmol m^{-2} s^{-1}, which is much larger than the estimated long-term mean emission rate of 6×10^{-3} nmol m^{-2} s^{-1} (see Table S.2) in the present study. This large discrepancy can be due to different emission/formation mechanisms of formic acid. For the dry savanna soil, emissions of formic acid may be caused by soil bacteria or physicochemical partitioning between the soil reservoir and the atmosphere. In our case, emissions are rather attributed to physicochemical processes on soil (more specifically, heterogeneous oxidation processes) instead of microbial activities and reservoir of the soil itself, due to the applied sterilization and flushing procedures on the soil sample prior to field experiment. To the best of our knowledge, this study is the first trial to evaluate the potential contribution of physicochemical processes on soil under real ambient conditions to the atmospheric budget of formic acid. Assuming the heterogeneous formation of formic acid also applies to other bare soil types around the globe, a global formic acid source strength of ~ 0.24 Tg yr^{-1} can be estimated using the average emission rate obtained here and a global barren land (i.e., bare soil and land with

very sparse vegetation) surface area of ~ 2.8×10^7 km^2 (Roser and Ritchie, 2018). This source strength due to heterogeneous reactions on bare soils is comparable to that from anthropogenic and biofuel emissions (0.4 Tg yr^{-1} by Millet et al., 2015) but still much less than the missing source strength. Note that the magnitude of the emission rate here used for calculation also depends on the mixing ratio levels of ambient VOC precursors and other environmental parameters such as temperature,

5   relative humidity and photochemistry on soil surfaces. Due to the design of our experimental setup, no sunlight reaches the soil surfaces (see Sect. 2.2). But one can imagine that the existence of sunlight would enhance the catalytic effect of soil minerals (e.g., titanium oxide) and, the soil surface will become hotter and thus make soil dry out faster. These changes may influence the exchange rates of the examined VOCs through the following ways: (1) high catalytic efficiencies may accelerate transformations of deposited VOC precursors and the formation/emission of formic acid; (2) high temperatures of soil may let

10   more adsorbed VOC molecules escape from soil surfaces through evaporation and decrease their uptake; (3) low amounts of water on soil may increase the uptake of some hydrophobic VOC species and decrease the uptake of some hydrophilic VOCs. The combined effect of these three aspects may even tell another different story, which deserves further studies. In a real soil situation, the physicochemical (i.e., abiotic) processes are often combined with biotic processes. The dominance of one over the other is influenced/controlled by changing environmental factors (i.e., temperature, relative humidity and photochemistry)

15   and/or soil types. However, here we assume that physicochemical processes on soil surfaces (more likely on soil solid phase through heterogeneous chemistry) can be a common phenomenon, which is occurring in parallel with biotic processes. Because the solid phase of soil, which includes minerals and organic matter (with minerals' content much higher than organic matter), are generally stable in nature (https://www.ctahr.hawaii.edu/mauisoil/a_comp.aspx). We think the results obtained in our study can provide a helpful reference regarding the potential contribution of soil particles to formic acid budget from a

20   physicochemical (heterogeneous chemistry) point of view, especially when the soil is dry and the microbial activities are low under some specific situations. Considering the still poorly understood budget of formic acid (Millet, 2012;Paulot et al., 2011), more investigations are needed to quantify the contributions of different types of soil as a potential source of formic acid under different environmental conditions.

25   Wind erosion of soil is an important pathway to generate mineral dust aerosols (Zender et al., 2011). Thus, our soil-based formic acid formation mechanism may also apply to soil-derived dust. Indeed, field measurements have identified formic acid to be among the most abundant carboxylic acids in collected mineral dust (Falkovich et al., 2004;Khare et al., 1998). However, dust was treated as a sink of gaseous formic acid in recent model simulations (with a simulated dust uptake of 1.2 Tg yr^{-1} in Millet et al., 2015;Paulot et al., 2011) based on laboratory-observed uptake of formic acid on clay minerals followed by fast

30   surface saturation (Hatch et al., 2007). Here, we may predict heterogeneous transformations of other co-adsorbed VOCs in the ambient air (e.g., formaldehyde) followed by emission of formic acid on dust, preferentially under low relative humidity conditions (Fig. 8). Based on our observed emission rate, a global emission strength can be roughly estimated by assuming that dust particles have a mean diameter of 2 μm and a density of 2.2 g cm^{-3} as adopted by Hatch et al. (2007). Using an average atmospheric dust loading of 18 Tg (Kok et al., 2017) would result in a formic acid source of ~ 2.4×10^{-5} Tg yr^{-1}. Note that

estimating the emission of dust aerosol particles, a 10000 times lower emission rate for formic acid should be applied to account for the real available surface (versus the geometric surface used here for soil, to reflect common model input needs). Clearly, this additional formic acid source on dust is much smaller and can be considered negligible. However, our observed formic acid emission to some extent challenges model applications of high initial uptake coefficients on clay minerals derived

5   from laboratory experiments; and previous model simulation may need to be re-constrained.

Aging of organic aerosols by heterogeneous reactions with OH radicals has been proposed as an important secondary source of formic acid (Molina et al., 2004;Paulot et al., 2011), and formic acid heterogeneous production was indeed observed during organic aerosol aging in the laboratory (Eliason et al., 2003;Molina et al., 2004;Walser et al., 2007;Vlasenko et al.,

10 2008;Malecha and Nizkorodov, 2016). Stavrakou et al. (2012) modelled the heterogeneous oxidation of organic aerosols as a source of formic acid assuming that one molecule of formic acid is formed per molecule of OH lost. They calculated an extra global annual formic acid flux of 27 Tg, which is still less that the missing source invoked to explain their remote sensing total column observations (see also Millet et al., 2015). However, based on high concentrations of reactive oxygen species (ROS) prevailing in atmospheric aerosol particles (Chung et al., 2006;Verma et al., 2015;Tong et al., 2016), we may consider more

15 VOC precursors being oxidized to formic acid than has been adopted in the model.

5 Conclusions

VOC heterogeneous chemistry at the gas-surface interface of soils play a central role in regulating atmospheric trace gas mixing ratios. In the present study, a coated-wall flow tube system coupled with a PTR-MS analysis was adopted to investigate the exchange of common VOC species at the atmosphere-soil interface at real-world ambient air conditions of an urban

20 background site in Beijing. Almost all VOCs show an average net deposition on the pre-treated sterilized soil, examined over an extended exposure of one month. The derived deposition velocities are found to be at the lower end of ranges reported for natural soil habitats, but were in fair agreement with models based on pure physicochemistry. Only formic acid displays a long-term emission. The net emission of formic acid is solely due to physicochemical processes (i.e., heterogeneous transformations of absorbed VOC precursors) on soil, which represents an additional ground-based source of this organic acid.

At ambient atmospheric conditions, both the relatively low uptake coefficients derived for the majority of VOC species and the emission of formic acid from the soil to some extent challenge the applicability of models using uptake coefficients derived from laboratory-based uptake measurements, where single VOC species or simple mixtures are supplied using purging air devoid of oxidizing agents. Field measurements as presented here, with all relevant parameters changing in concert, may call

30 attention to the existence of yet unknown interferences or synergetic effects.

As our soil sample is sterilized, the uptake and emission characteristics observed in this study can reflect the contribution of abiotic processes in soil regarding VOC exchange at the atmosphere-soil interface. However, natural soils are a complex ecosystem including leaf litter, plant roots, microorganisms and soil particles. Taking the biotic processes and different soil types into account may produce different results from we observed here. Previous studies have shown that soil can be a source

5 of short-chain oxygenated VOCs and terpenes due to emissions of soil vegetation (e.g., grass and crops), degradation of leaf litter and other activities of soil living organisms (Schade and Goldstein, 2001;Hayward et al., 2001;Gray et al., 2010;Chen et al., 2004;Lin et al., 2007;Scholler et al., 2002;Rossabi et al., 2018). For example, Leff and Fierer (2008) found that litter samples could produce more types of VOCs than the soil samples without litter covers, indicating degradation of soil litter can be an important source of VOC emission. On the other hand, other studies have observed deposition of several categories of

10 VOCs (e.g., alcohols, aldehydes and monoterpenes) on various types of soils (Asensio et al., 2007a;Asensio et al., 2008;Aaltonen et al., 2013;Gray et al., 2014). Considering that the results obtained in the present study can only address the effects of physicochemical processes on VOC exchange, follow-up studies are needed to explore the contribution of soil living organisms (e.g., bacteria, fungi) to VOC exchange at the soil-atmosphere interface.

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List of Tables:

Table 1. List of reported VOC species along with their protonated m/z, and 5-minute limits of detection (LOD).

Protonated (m/z)	Species	LOD (ppt)	Protonated (m/z)	Species	LOD (ppt)
21	$H_3^{18}O^+$		69	isoprene	70
39	$H_3^{18}O^+$ (H_2O)		71	MVK+MACR	109
31	formaldehyde	101	73	MEK	198
33	methanol	355	79	benzene	78
42	acetonitrile	87	93	toluene	93
45	acetaldehyde	112	105	styrene	55
47	formic acid	277			
59	acetone	77			
61	acetic acid	243			

MVK: methyl vinyl ketone; MACR: methacrolein; MEK: methyl ethyl ketone.

Table 2. Parameters used for resistance calculations to infer the relative importance of R_c versus R_a and R_b, and the resulting deposition velocities (V_d) of measured VOC species.

VOCs species	γ ($\times 10^{-7}$)	ω (cm s^{-1})	D (cm^2 s^{-1})	u_* (cm s^{-1}) 1	2	3	z_0 (cm) 1	2	3	R_c (s cm^{-1})	R_a (s cm^{-1}) 1	2	3	R_b (s cm^{-1}) 1	2	3	V_d (cm s^{-1}) 1	2	3
Styrene	12.30	24636	0.08	30	45	20	10	100	4	132	0.67	0.32	1.12	0.27	0.18	0.40	0.008	0.008	0.007
Formaldehyde	8.92	45870	0.17	30	45	20	10	100	4	98	0.67	0.32	1.12	0.15	0.10	0.23	0.01	0.01	0.01
Toluene	6.74	26194	0.08	30	45	20	10	100	4	227	0.67	0.32	1.12	0.26	0.17	0.38	0.004	0.004	0.004
Isoprene	6.06	30468	0.09	30	45	20	10	100	4	217	0.67	0.32	1.12	0.24	0.16	0.36	0.005	0.005	0.005
Acetic acid	5.77	32435	0.12	30	45	20	10	100	4	214	0.67	0.32	1.12	0.20	0.13	0.30	0.005	0.005	0.005
MVK+MACR	4.80	30029	0.10	30	45	20	10	100	4	278	0.67	0.32	1.12	0.23	0.15	0.35	0.004	0.004	0.004
Acetaldehyde	3.63	37876	0.13	30	45	20	10	100	4	291	0.67	0.32	1.12	0.19	0.12	0.28	0.003	0.003	0.003
Methanol	3.43	44414	0.16	30	45	20	10	100	4	263	0.67	0.32	1.12	0.16	0.11	0.24	0.004	0.004	0.004
MEK	2.27	29609	0.09	30	45	20	10	100	4	595	0.67	0.32	1.12	0.23	0.16	0.35	0.002	0.002	0.002
Acetone	2.16	32990	0.11	30	45	20	10	100	4	561	0.67	0.32	1.12	0.21	0.14	0.32	0.002	0.002	0.002
Acetonitrile	2.12	39237	0.16	30	45	20	10	100	4	480	0.67	0.32	1.12	0.17	0.11	0.25	0.002	0.002	0.002
Benzene	1.89	28448	0.09	30	45	20	10	100	4	745	0.67	0.32	1.12	0.24	0.16	0.36	0.001	0.001	0.001
Formic acid	-2.15	37044	0.15	30	45	20	10	100	4	-502	0.67	0.32	1.12	0.17	0.12	0.26	-0.002	-0.002	-0.002

γ: uptake coefficient; ω: mean molecular speed at 25 °C; D: molecular diffusion coefficient at 25 °C; u_*: friction velocity, the listed values are averaged between the day and night cases by Zhang et al., (2003); z_0: aerodynamic surface roughness length, the listed values are referred to Zhang et al., (2002); R_c: soil surface resistance; R_a: aerodynamic resistance, calculated using the equation (19.14) in (Seinfeld and Pandis, 2016), where the reference height z is set as 300 m; R_b: quasi-laminar layer resistance, calculated using the equation (19.17) in (Seinfeld and Pandis, 2016), where the air kinematic viscosity ν is 0.16 cm^2 s^{-1}; V_d: deposition velocity; The numbers in the table header denote different land use categories adopted from Zhang et al., (2002; 2003): 1 shrubs; 2 urban; 3 barren land (mostly desert).
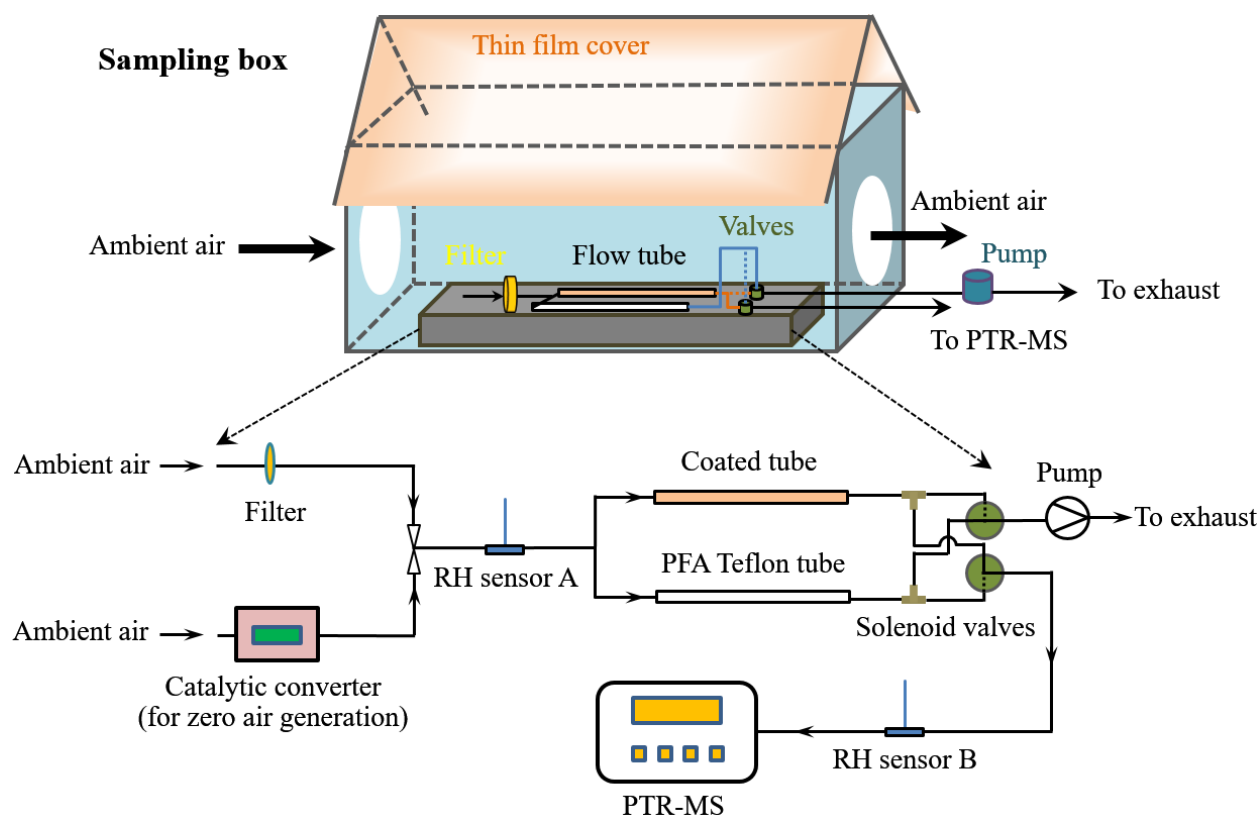
Figure 1. Schematic illustration of the experimental setup.
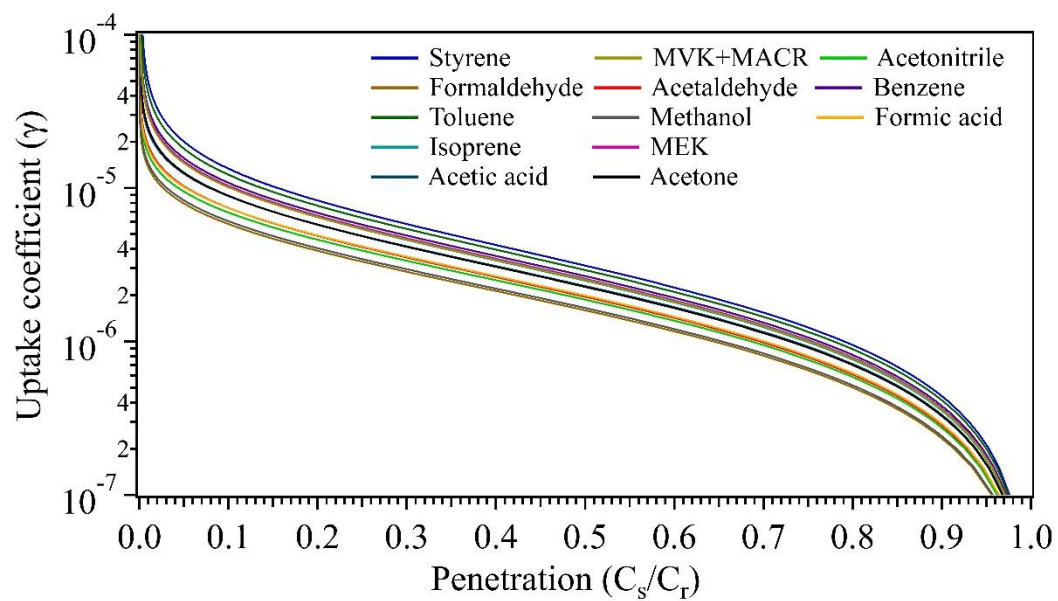
Figure 2. Schematic of the uptake coefficients versus the penetrations of measured VOC species. Derivation of the uptake coefficients are based on the experimental parameters: volumetric flow rate F = 0.1 L min^{-1} at 1 atm and 298 K; coated-wall flow tube dimension, d = 1.6 cm, L = 10 cm.
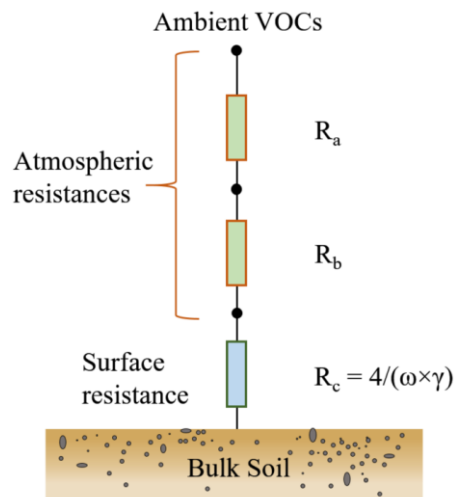
Figure 3. Schematic of the resistance model for VOC species dry deposition on soil. R_a: aerodynamic resistance; R_b: quasi-laminar layer resistance; R_c: soil surface resistance.
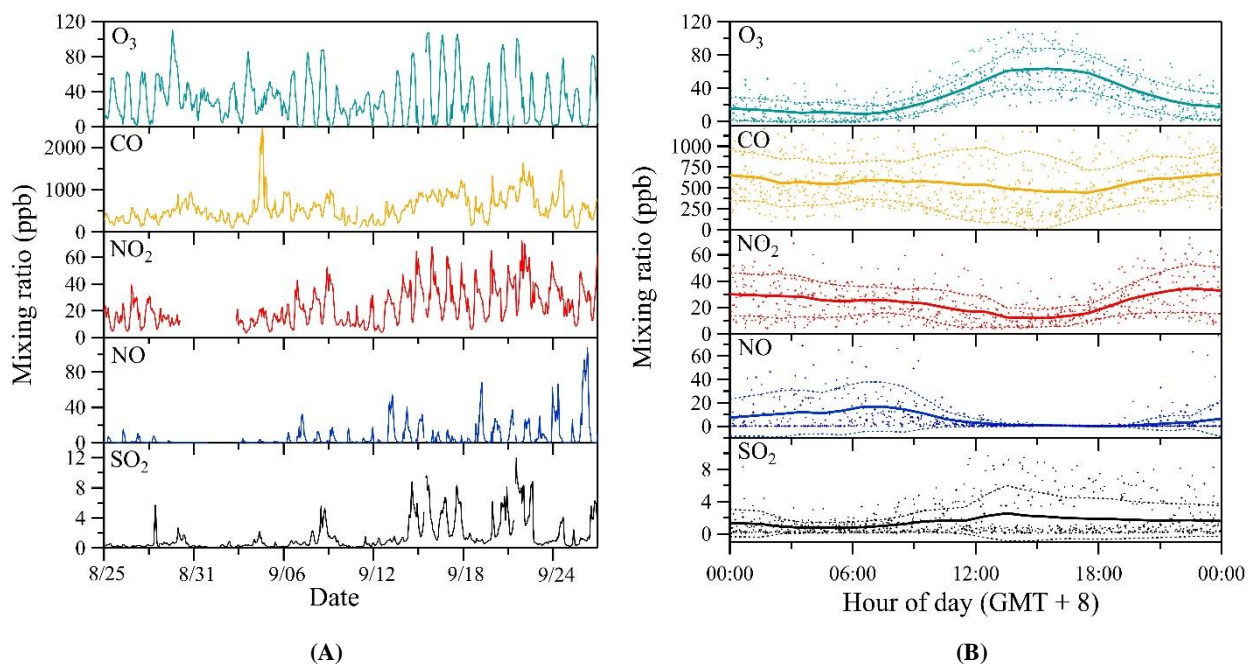
Figure 4. Time series of observed ambient air mixing ratios of prominent gas phase pollutants (A) and respective mean diel courses (B). In (B), symbols denote individual hourly averaged data, and the thick solid lines respective mean diel profile. Thin dashed lines represent one standard deviation (± 1 SD) from the mean value.
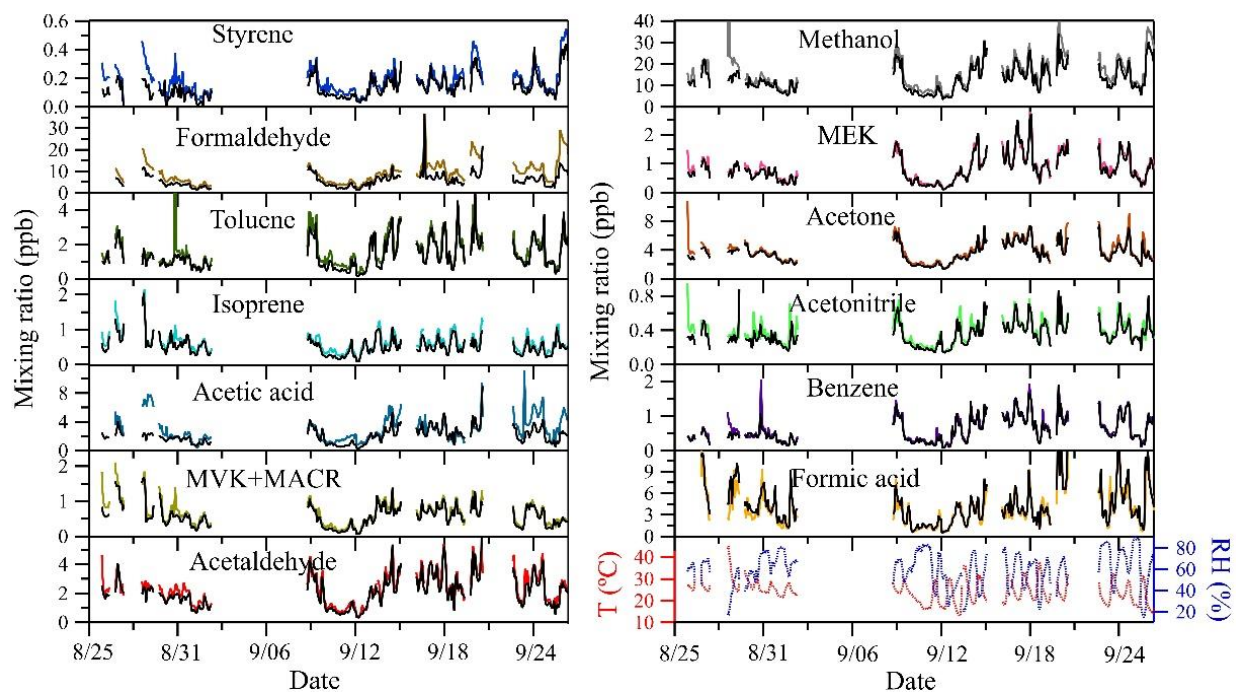
Figure 5. (A)
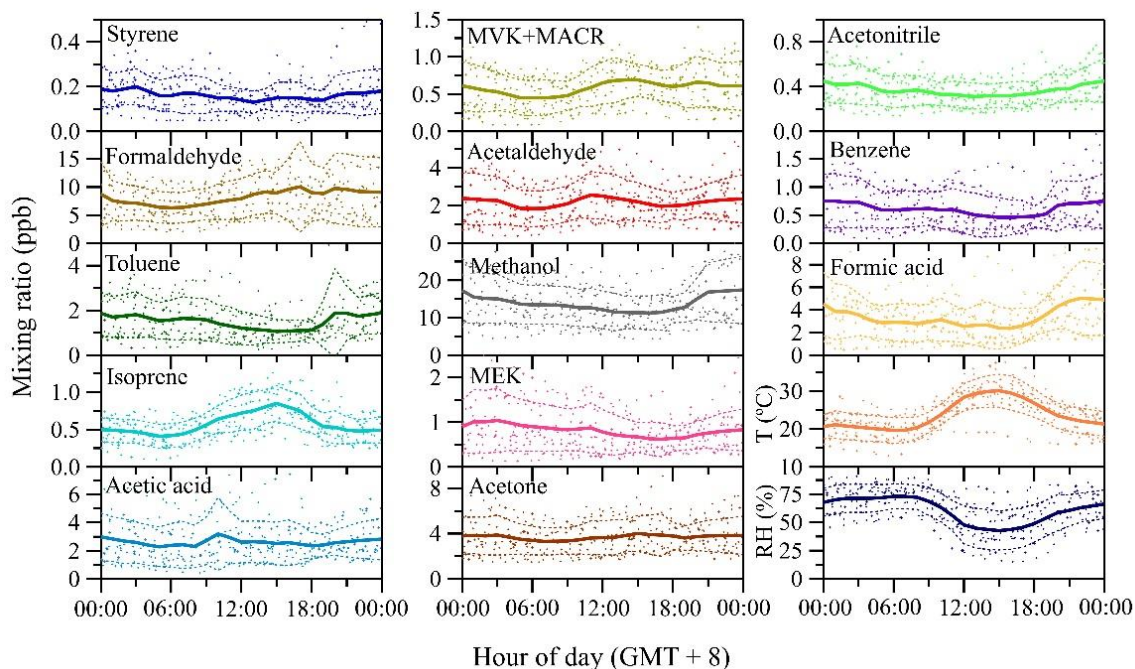
Figure 5. (B)

Figure 5. Time series of observed ambient air mixing ratios of VOCs and air temperature and relative humidity (A), and respective mean diel courses (B). Colorful lines in (A) denote ambient air mixing ratios at the outlet of the reference tube C_r, and black lines at the outlet of the sample tube C_s. In (B), symbols denote individual hourly averaged data, and the thick solid lines respective mean diel profile. Thin dashed lines represent one standard deviation ($\pm$ 1 SD) from the mean value.
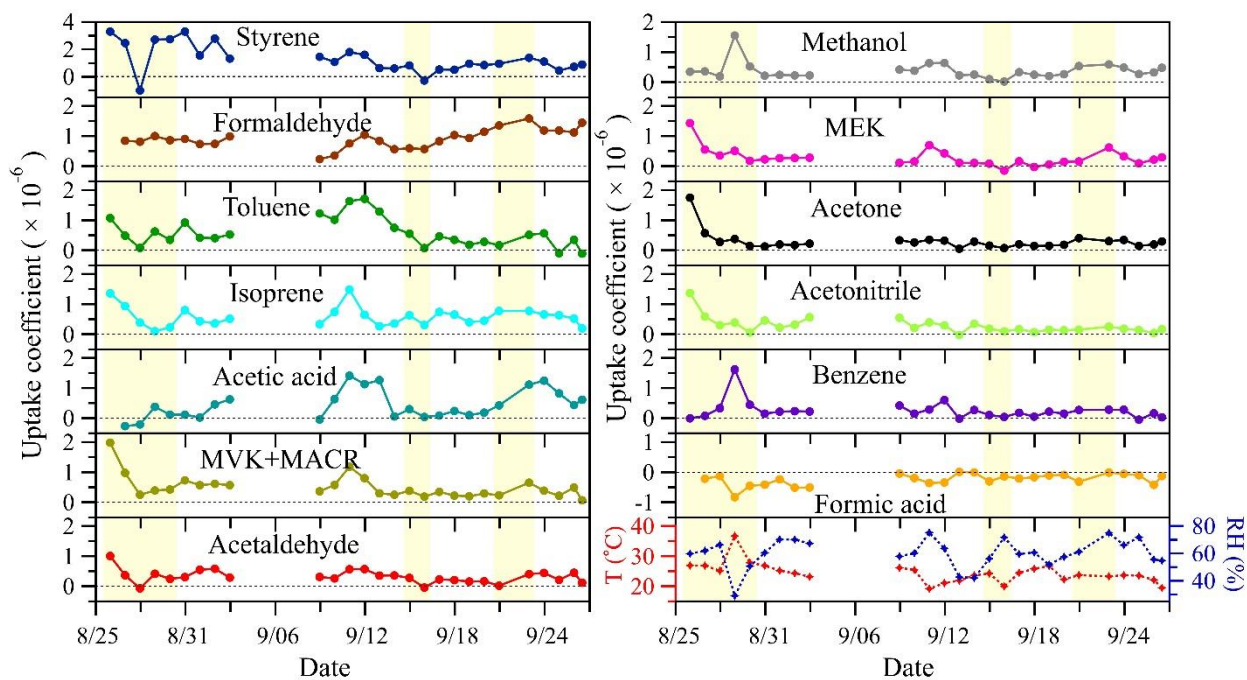
Figure 6. (A)
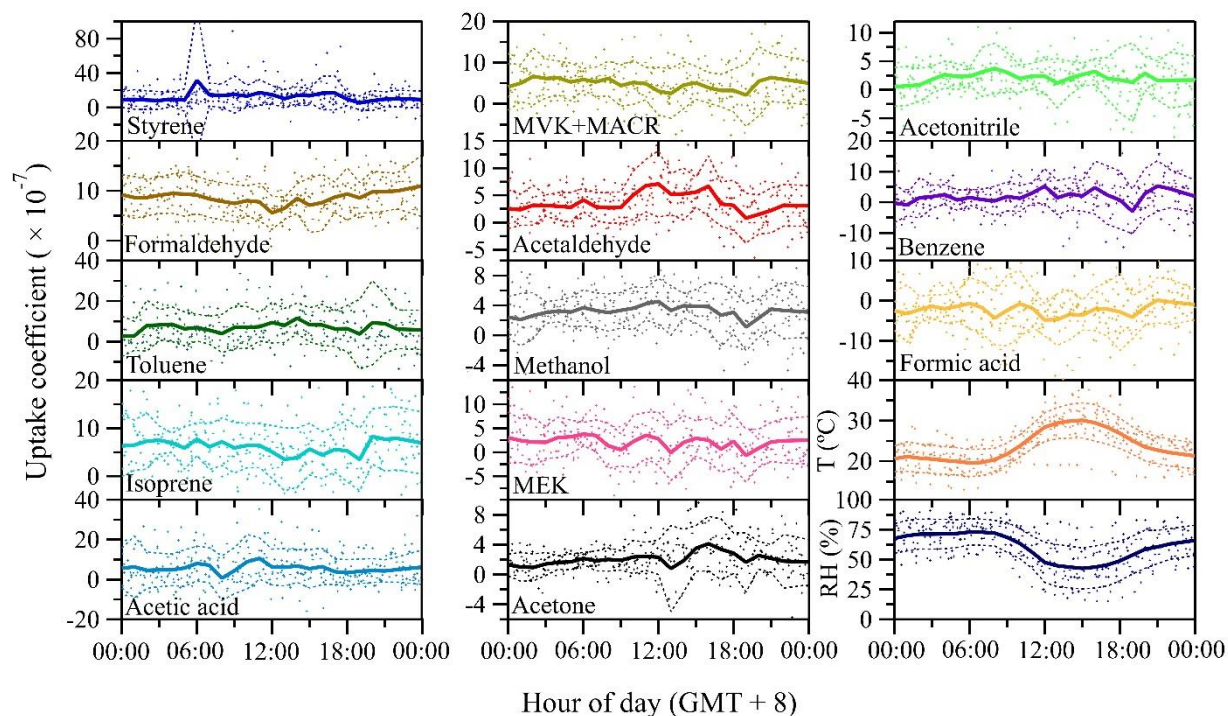
Figure 6. (B)

Figure 6. Time series of the uptake coefficients of measured VOC species and air temperature and relative humidity (A), and respective
5   mean diel courses (B). In (A), each symbol represents daily averaged data and the yellow shaded areas indicate the days when measurements
were not continuously running all day long. In (B), symbols denote individual hourly averaged data, and the thick solid lines respective mean
diel profiles. Thin dashed lines represent one standard deviation (± 1 SD) from mean values.
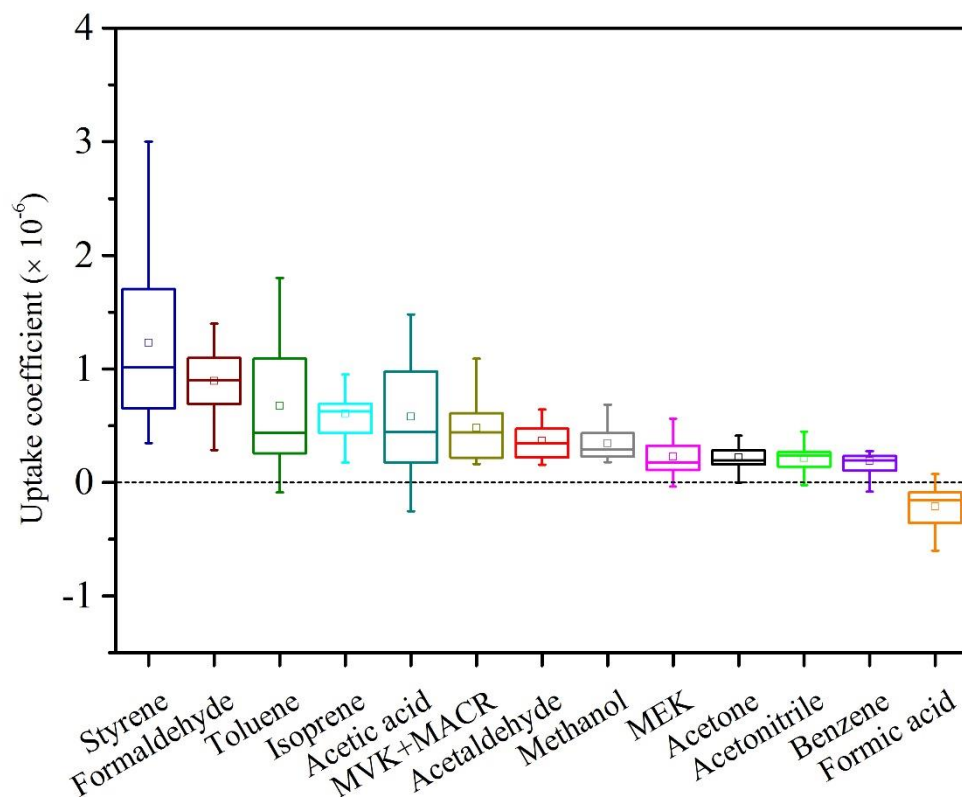
Figure 7. Box-and-whisker plots of the uptake coefficients of measured VOC species, based on daily averaged data. Minimum, 25th, 50th,
75th percentile and maximum are indicated by bars, and mean values by squares.
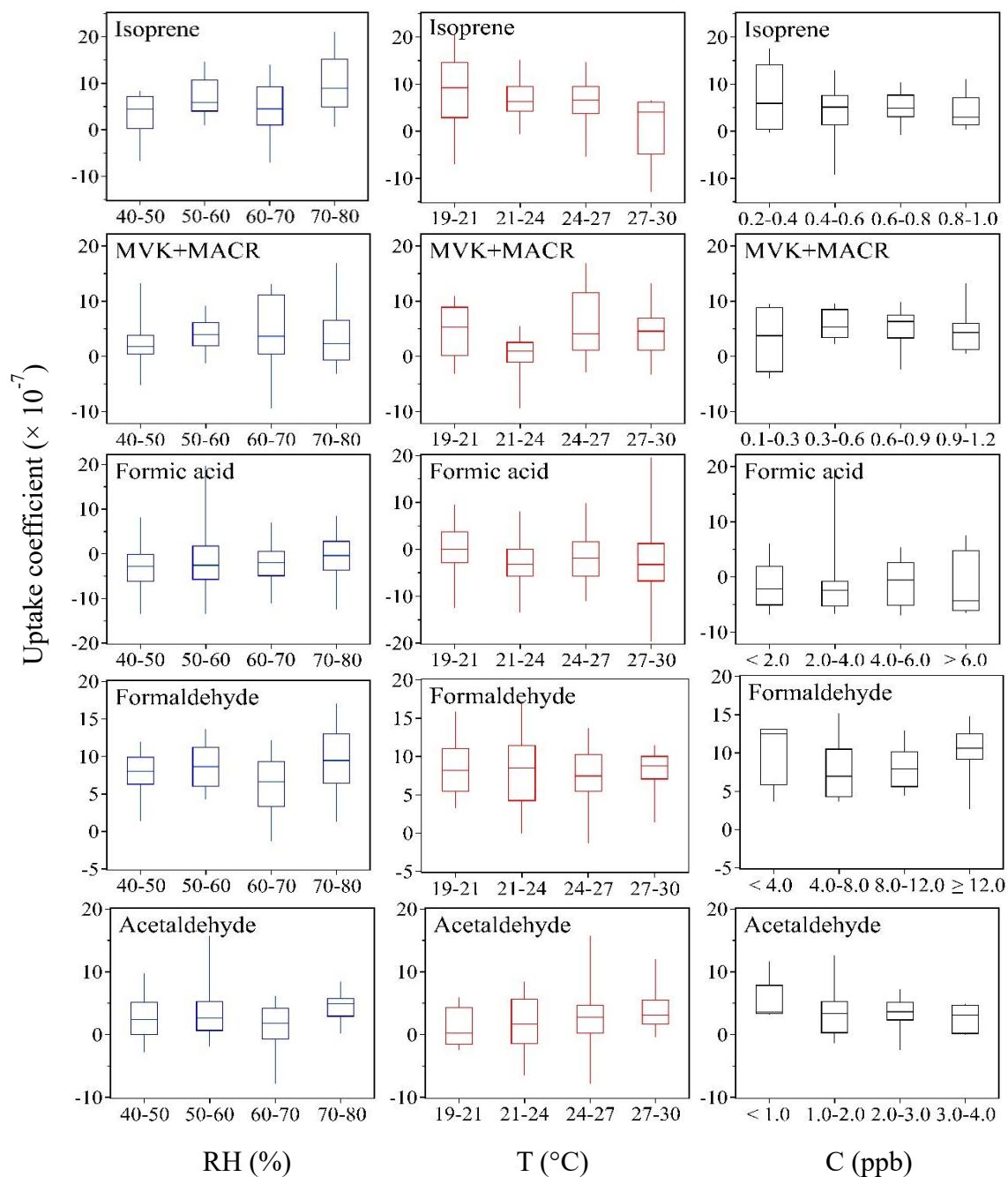
Figure 8. Dependence of uptake coefficients on ambient relative humidity (RH), temperature (T) and mixing ratios (C). Minimum, 25th, 50th, 75th percentile and maximum of the box-and-whisker plots are indicated by bars. The uptake coefficient dependence is based on the hourly averaged data, and the RH and T dependences are plotted when C is varied within a very narrow range (nearly constant) and C dependence is plotted when RH equals to 50%. Note that negative uptake coefficients indicate emission. For details see text.
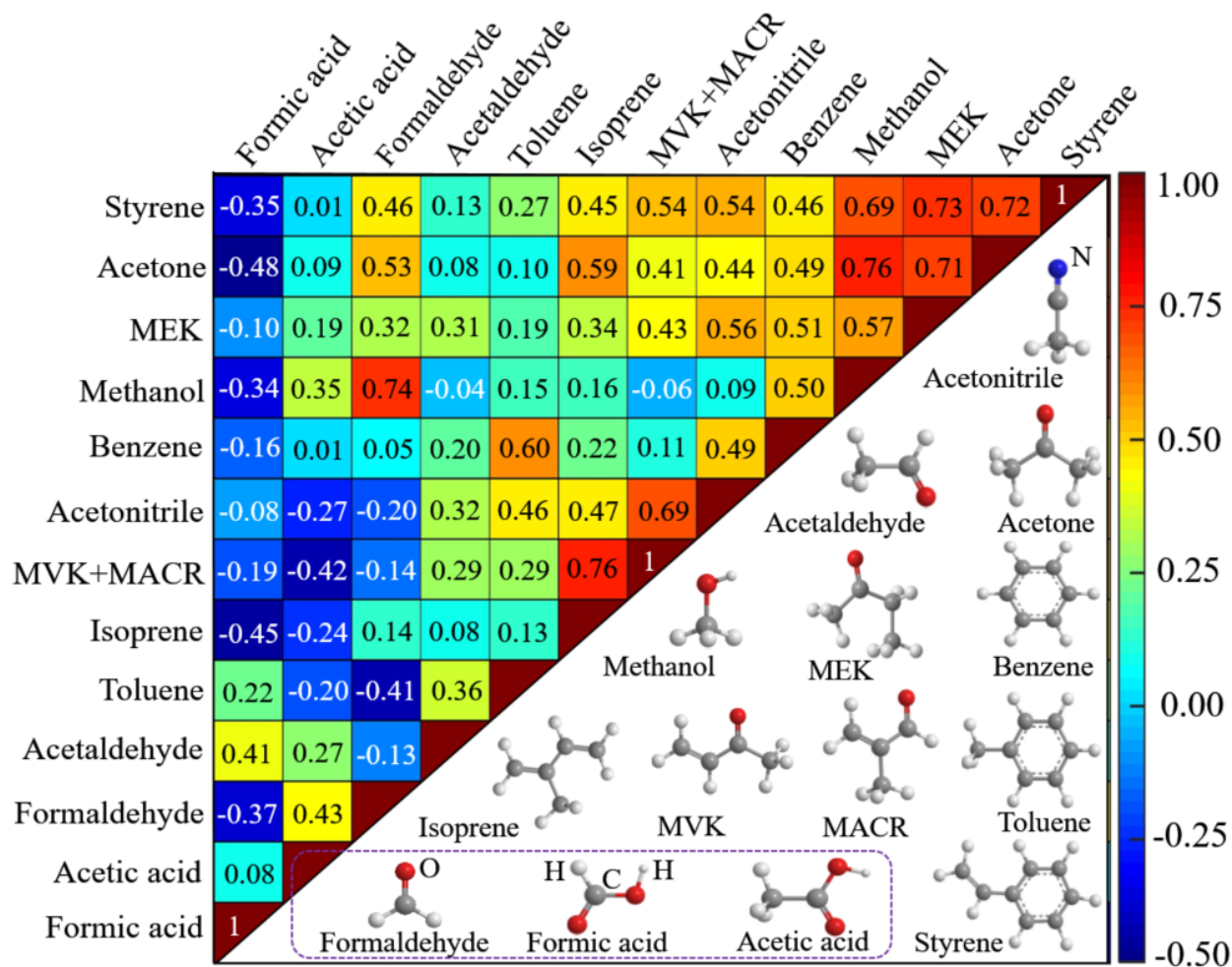
Figure 9. Correlation of the exchange of measured VOC species (upper left) and their molecular structures (lower right). Correlation between each pair of VOCs is reflected by the correlation coefficient, shown in the plot. The correlation coefficient between each individual species itself is 1, a correlation coefficient of 0 means no correlation, and -1 implies complete anti-correlation.