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Wheat straw return can lead to biogenic toluene emissions

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ARTICLE INFO

Article history:

Received 12 April 2021

Revised 18 August 2021

Accepted 30 August 2021

Available online 2 February 2022

Keywords:

Toluene

Biogenic volatile organic compounds (BVOCs)

Emission profile

Straw return

ABSTRACT

As a common practice in agricultural system, straw return has been reported to release a large number of trace gases and attracted much attention. However, the role of straw return in toluene emission remains poorly understood. In this study we measured the emissions of toluene as well as other 50 volatile organic compounds (VOCs) from wheat straw return for 66 days under flooded and non-flooded conditions, respectively. The results showed that substantial toluene was released from the returned wheat straw particularly under flooded condition, and primarily derived from the secondary product. Toluene emissions from the returned wheat straw were 36.8 and 8.45 mg C/kg, sharing 28.0% and 8.6% of total VOCs released, and over 90% of toluene emissions occurred between days 24–56 and 0–17 under flooded and non-flooded conditions, respectively. The emission rates of toluene were relatively high but decreased sharply at the beginning 2 days, and then was steady until 24 days under the two moisture conditions. After the initial decrease these rose again to form one “peak emission window” between days 24–56 under flooded condition, while these were still very low and steady until the end under non-flooded condition. The toluene emission rates significantly positively correlated with microbial biomass C under flooded condition, but negatively associated with bacteria and fungus number, microbial biomass C, and CO₂ flux under non-flooded condition, suggesting that microorganism might play an important role in toluene emissions from wheat straw return. A rough estimate indicated that straw return might be important for biogenic toluene.

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Introduction

Toluene is a ubiquitous and abundant aromatic compound observed in the troposphere (Zou et al., 2015; Zhang et al., 2016). It has received special attention due to its important roles in

atmospheric chemistry and adverse health effects. As a very reactive gas in the atmosphere, toluene is readily oxidized to produce tropospheric ozone (O₃) (Russell et al., 1995) and secondary organic aerosol (SOA) (Odum et al., 1997; Li et al., 2016), and thus plays a critical role in photochemical smog and fine particle pollution (Zou et al., 2015; Ding et al., 2017). As a hazardous pollutant, it can also be harmful to humans, causing brain function disturbances and affecting the neurological and endocrine systems (ATSDR, 2017).

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Toluene, as a major constituent of petroleum, is emitted into the atmosphere. Its presence in the atmosphere is generally assumed to derive solely from anthropogenic sources (Zou et al., 2015; Zhang et al., 2016; Ding et al., 2017). However, recent studies have shown that biogenic sources also contribute substantially to toluene in the atmosphere, with the global annual emissions of 0.32–1.37 Tg C/year (Sindelarova et al., 2014; Misztal et al., 2015; Cabrera-Perez et al., 2016; Henrot et al., 2017). Global SOA formation from biogenic toluene (0.3–3.0 Tg/year) could be equal in importance to that from anthropogenic toluene (0.6–4.5 Tg/year) (Misztal et al., 2015) because SOA yields from toluene are much higher under low NO_x conditions in the atmosphere compared with under polluted high NO_x conditions (Li et al., 2016).

Plants are the dominant biogenic source of toluene in the atmosphere, and the toluene emissions from living vegetation have attracted more and more attention (Heiden et al., 1999; Holzinger et al., 2000; White et al., 2009; Misztal et al., 2011, 2015; Rantala et al., 2015; Paralovo et al., 2016). Vegetation (e.g., leaves, flowers, and phytoplankton) release toluene into the atmosphere at substantial rates, particularly under stress conditions or during flowering and phytoplankton bloom (Misztal et al., 2015). In addition to living vegetation, various plant litters contain toluene when they just fall on the floor, and can also release a certain amount of toluene during the degradation (Isidorov et al., 2003; Fedele et al., 2007). So far, only limited laboratory measurements have quantified toluene emissions from forest and grassland plant litters (Isidorov et al., 2003; Fedele et al., 2007; Gray et al., 2010). In a laboratory experiment on volatile organic compound (VOC) emissions from leaf litter of deciduous trees, Isidorov et al. (2003) found that toluene emissions from leaf litters of *Pinus sylvestris* and *Picea exelsa* after storage for 4 weeks increased from 2.4% to 5.0% and from 0% to 2.3% of the total VOC emissions, respectively. Fedele et al. (2007) observed that total VOC emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak) in the 30 and 20 hr following cutting in laboratory, respectively, reached 0.38 ± 0.04 and 0.022 ± 0.003 g/kg. Gray et al. (2010) obtained that toluene emissions, respectively, were 0.58–358 and 0.76–221 mg C/kg during the biotic and abiotic decomposition of litter from 12 plant species over a 20-day laboratory incubation period. The available data suggest that dead plant litters is a large source of toluene emissions, and vary with litter types as well as incubation conditions (Isidorov et al., 2003; Fedele et al., 2007; Gray et al., 2010).

The annual global production of agricultural residues is approximately 2.9×10^9 tons (FAO, 2020), a large proportion of which are returned into the soil worldwide as a way of sustainable agriculture (Liu et al., 2014). Recent studies suggested that the returned agricultural residues can emit a large number of trace gases and thus contribute substantially to trace gases in the atmosphere such as CO₂, CH₄, VOCs and so on (Wang et al., 2015; Hu et al., 2016; Zhang et al., 2018). Accordingly, the release of abundant toluene from the returned straw would be expected during the decay process. However, to date, few study has been performed on the toluene emissions from crop residues decayed in agricultural soils, except that Zhang et al. (2018) conducted a field experiment study in a straw-returned maize cropping system. Thus, more mea-

surements are needed to accurately evaluate the contribution of straw return on toluene emissions and fully understand its underlying mechanism.

Considering that microbial production and decomposition (Ramirez et al., 2010), abiotic physicochemical degradation, absorption by soil mineral particle surfaces or organic matters and dissolution in soil solutions occur simultaneously (Peñuelas et al., 2014), the toluene emissions from plant residues returned in soils are a consequence of production, degradation and transport of this compound into the soils. This process is strongly influenced by environmental conditions such as soil moisture owing to the difference in oxygen supply, microbial community composition and amount as well as gas diffusion (Svendsen et al., 2016; Zhang et al., 2018). We assumed that the toluene emission change with the water content in soil. In this study, the emissions of toluene and other VOCs as well as related microbial parameters were investigated during the decomposition of wheat residues returned in agricultural soil under flooded and non-flooded conditions, respectively. It is hypothesized that the occurrence of straw amendment acts as a significant source of toluene production, which subsequently emits to the atmosphere. These results will draw attentions to the emission profiles of toluene from the returned straw during the decay process, and contribute to a better understanding the impact of straw return on atmospheric toluene.

1. Materials and methods

1.1. Soil and straw collection

The soil and straw (*Triticum aestivum*) used in the experiment were collected from a typical subtropical paddy field under rice-wheat crop rotation in Wuhu, China (N 31° 16.804', E 118° 35.164'). Mineral soils were collected from the top 5 cm of the profile. The soil is loamy sand with a pH of 5.18 and a water holding capacity of 80%, containing a total-C of 18 g/kg, total-N of 1.5 g/kg, total-S of 1.7 g/kg, available-S of 36.8 mg/kg, and available-P of 7.35 mg/kg. After collection, the soil was air-dried, grounded, and passed through a 2 mm sieve, and then stored under cool and dry conditions. Fresh wheat straw was collected immediately after harvesting in May 2013. The straw characteristics were as follows: total-C content of 395 g/kg, total-N content of 4.5 g/kg, total-S content of 0.65 mg/kg, and water content of 7%. After collection, the wheat straw was cut into 0.5 cm length for use.

1.2. Experimental design

The experiment was performed in a laboratory and the equipment used is described in detail elsewhere (Wang et al., 2015). Briefly, self-made reactors were used to incubate wheat straw in agricultural soils, each being made of a cubic box (35 cm × 35 cm × 35 cm) without a cover, but with a collar. Dynamic chambers (35 cm × 35 cm × 15 cm) were used to collect gas samples, each containing an air inlet, an air outlet, and two small fans for mixing headspace air. Both the reactor and chamber were made of stainless steel plates, with their in-

ner walls coated with Teflon films. All of the connecting tubes were made of Teflon.

Microcosms containing soil alone or supplemented with wheat straw were cultivated for 66 days and sampled on days 0, 2, 4, 7, 12, 17, 24, 34, 44, 56, and 66. A total of 4 treatments were conducted, each in triplicate: (1) soil amended with wheat straw under flooded condition; (2) soil amended with wheat straw under non-flooded condition; (3) soil alone under flooded condition as the flooded control; and (4) soil alone under non-flooded condition as the non-flooded control. 27 kg of dry paddy soil was filled into each incubator in the two control groups, while 28.35 kg of dry straw-soil mixtures (1:20) were put into each reactor in the two experimental groups. Distilled water was added into each incubator in order to adjust the water holding capacity (WHC) of soils or straw-soil mixtures to 80% for non-flooded groups and the water depth to 8 ± 2 cm for flooded groups. All of the treatments were incubated at room temperature ($25 \pm 0.5^\circ\text{C}$). Except for sampling, the reactors were exposed to air. Measurements were simultaneously conducted on toluene and other VOCs, CO_2 , as well as microbial biomass C, population, and communities during the experiment.

1.3. Lab analysis

Toluene as well as other VOCs in the air sample were analyzed using an Entech 7100 preconcentrator (Entech Instruments Inc., CA, USA) coupled with an Agilent 5973 N gas chromatography-mass selective/flame ionization detector (GC-MS/FID, Agilent Technologies, USA). Sample analysis, standard preparation, and calibration were similar to those reported previously (Wang et al., 2015; Zhao et al., 2016). Briefly, toluene and other VOCs in the air samples were concentrated using an Entech preconcentrator with three stages of cryotrapping, and then transferred into the GC-MS/FID system for analysis. The mixture was firstly separated by a HP-1 capillary column ($60 \text{ m} \times 0.32 \text{ mm} \times 1.0 \mu\text{m}$, Agilent Technologies, USA) with helium as the carrier gas, and then split into two ways: one is to a PLOT-Q column ($30 \text{ m} \times 0.32 \text{ mm} \times 20 \mu\text{m}$, Agilent Technologies, USA) followed by flame ionization detector (FID); another is to a $65 \text{ cm} \times 0.10 \text{ mm}$ inside diameter (ID) stainless steel line followed by mass spectrum detector (MSD). The GC oven temperature was programmed to be initially at -10°C , holding for 3 min, increasing to 120°C at $5^\circ\text{C}/\text{min}$, and then to 250°C at $10^\circ\text{C}/\text{min}$, and holding for 10 min. The MSD was used in scan mode with the mass range from 35–350 amu, and the ionization method was electron impacting (EI). Target compounds were identified based on their retention times and mass spectra, and quantified using an external calibration method. All VOCs except C_2 – C_3 non-methane hydrocarbons (NMHCs) were determined based on MSD signals. For C_2 and C_3 NMHCs, they were detected based on FID signals. The quality assurance and control (QA/QC) process is elaborated in Appendix A Supplementary data.

Microbial biomass C was measured by chloroform fumigation-extraction as described in a previous study (Vance et al., 1987). CO_2 was measured using a HP 4890D GC (Agilent Technologies, USA) coupled with a FID as described elsewhere (Wang et al., 2015). Bacterial, fungal, and actinomyces isolation, identification, and count were based on

plate dilution using a culture medium of beef extract peptone agar, potato dextrose agar (PDA), and Gause I, respectively (Atlas, 1993).

1.4. Flux measurement

The emission fluxes of toluene, other VOCs, and CO_2 were measured using a dynamic flow-through chamber technique as described elsewhere (Wang et al., 2015). Briefly, dry clean air (with toluene and CO_2 levels comparable to those in ambient air) from a gas cylinder instead of ambient air passed through the chamber after being humidified by deionized water at a rate of 0.5 L/min. After 4 hr (over 5 cycles of residence time) when a steady state was reached, air samples were collected from the outlet with 1 L Teflon sampling bags (SKC Inc., USA). The emission fluxes (F_e , $\mu\text{g C}/(\text{kg}\cdot\text{hr})$) were calculated as:

$$F_e = Q \times (C_o(t) - C_i(t))/M_w \quad (1)$$

where Q (L/hr) is the airflow rate of compressed air through the chamber, $C_o(t)$ ($\mu\text{g C}/\text{L}$) is the concentration in the outgoing air, and $C_i(t)$ ($\mu\text{g C}/\text{L}$) is the concentration in the incoming air. For toluene, other VOCs, and CO_2 , $C_i(t)$ is the level in the gas cylinder. M_w (kg) is the dry mass of straw-soil mixture or straw alone in the test groups and soil alone in the control groups.

1.5. Statistical analysis

To evaluate the differences in toluene emissions and microorganisms between the two test treatments, these data were tested using one-way analysis of variance (ANOVA) with a post hoc least significant difference (LSD) test. Regression analysis was performed to investigate the relations of toluene fluxes to microbial biomass C, respiration rate, and population. The criterion for significance that was used in all statistical tests was $p < 0.05$.

2. Results and discussion

2.1. Contribution of toluene to total VOCs

Table 1 shows VOCs released from the soil alone and the straw returned in the soil during the 66-day incubation period under the two moisture conditions. In total, fifty-one VOCs were identified and quantified, namely eleven NMHCs, thirty-five oxygenated VOCs (OVOCs), four sulfides and one halohydrocarbon, during the 66-day incubation period. The total VOC emissions from the returned straw in the two test groups were over 10 times higher than those in their corresponding control groups, indicating that the incorporated straw was a source of VOCs. The OVOCs and NMHCs dominated, contributing 68.9% and 31.0% of the total VOCs in the flooded test treatment and 84.9% and 14.9% in the non-flooded test treatment, respectively. Top 10 VOCs released from the amended straw in the two test treatments were ethene, propene, toluene, ethanol, *i*-propanol, 2-butanol, acetone, 2-butanone, 2-pentanone and acetophenone, altogether accounting for over 92% of the total emitted VOCs (Table 1). Acetone was the most abundant and shared 33.7% and 58.9% of the total VOCs in the flooded

Table 1. – VOC emission mass ($\mu\text{g C/kg}$) during the incubation in the four groups.

| Compounds | Flooded test group | | Non-flooded test group | | Flooded control group | Non-flooded control group |
|-------------------------|--------------------|--------------|------------------------|--------------|-----------------------|---------------------------|
| Ethane | 67.5 ± 8.89 | 3.21 ± 0.42 | 24.6 ± 3.12 | 1.17 ± 0.15 | 5.26 ± 1.36 | 2.09 ± 0.62 |
| Propane | 693 ± 11.4 | 33.0 ± 0.54 | 415 ± 79.1 | 19.8 ± 3.77 | 17.0 ± 6.70 | 6.20 ± 1.97 |
| n-Butane | 58.6 ± 8.14 | 2.79 ± 0.39 | 89.4 ± 15.3 | 4.26 ± 0.73 | 12.2 ± 3.43 | NE |
| i-Butane | 374 ± 2.65 | 17.8 ± 0.13 | 379 ± 59.3 | 18.1 ± 2.83 | 8.08 ± 2.46 | 0.68 ± 0.24 |
| n-Pentane | 640 ± 65.1 | 30.5 ± 3.10 | 813 ± 106 | 38.7 ± 5.04 | 9.15 ± 4.41 | NE |
| Ethene | 1313 ± 152 | 62.5 ± 7.23 | 1345 ± 218 | 64.0 ± 10.4 | 2.67 ± 0.94 | 1.47 ± 0.39 |
| Propene | 512 ± 38.6 | 24.4 ± 1.84 | 1869 ± 212 | 89.0 ± 10.1 | 1.31 ± 0.75 | 1.56 ± 0.36 |
| 1-Butene | 168 ± 20.3 | 8.00 ± 0.97 | 767 ± 110 | 36.5 ± 5.23 | 0.67 ± 0.42 | 1.80 ± 0.78 |
| 1-Pentene | 71.8 ± 4.43 | 3.42 ± 0.21 | 266 ± 75.5 | 12.7 ± 3.60 | NE | NE |
| Isoprene | 96.1 ± 5.50 | 4.58 ± 0.26 | 228 ± 19.2 | 10.9 ± 0.92 | 1.80 ± 0.79 | NE |
| Toluene | 36819 ± 5411 | 1753 ± 258 | 8451 ± 1539 | 402 ± 73.3 | NE | NE |
| Ethanol | 13646 ± 3018 | 650 ± 144 | 1942 ± 5678 | 92.5 ± 270 | 304 ± 89.3 | 18.7 ± 8.74 |
| i-Propanol | 5060 ± 887 | 241 ± 42.2 | 3384 ± 449 | 161 ± 21.4 | 142 ± 93.6 | NE |
| 1-Butanol | 252 ± 577 | 12.0 ± 27.5 | -617 ± 237 | -29.4 ± 11.3 | 6.68 ± 4.86 | 7.90 ± 3.24 |
| 2-Butanol | 1928 ± 461 | 91.8 ± 22.0 | 641 ± 37.8 | 30.5 ± 1.80 | NE | NE |
| i-Butanol | 251 ± 99.4 | 12.0 ± 4.73 | 112 ± 3.82 | 5.32 ± 0.18 | 10.5 ± 5.37 | 5.87 ± 3.51 |
| 2-Ethyl-1-hexanol | 1052 ± 663 | 50.1 ± 31.5 | 740 ± 396 | 35.2 ± 18.9 | -0.09 ± 0.06 | 9.32 ± 4.74 |
| Acetaldehyde | 848 ± 227 | 40.4 ± 10.8 | 391 ± 65.9 | 18.6 ± 3.14 | 7.76 ± 6.23 | 21.6 ± 7.40 |
| Butanal | 67.2 ± 11.4 | 3.20 ± 0.54 | -40.9 ± 32.4 | -1.95 ± 1.54 | -0.91 ± 0.52 | 26.3 ± 9.44 |
| i-Butanal | 95.4 ± 17.5 | 4.54 ± 0.83 | 82.0 ± 53.8 | 3.91 ± 2.56 | -0.08 ± 0.06 | 9.91 ± 5.28 |
| Pentanal | 72.7 ± 15.3 | 3.46 ± 0.73 | 44.3 ± 34.8 | 2.11 ± 1.66 | -1.11 ± 0.88 | 6.98 ± 4.33 |
| i-Pentanal | 60.6 ± 32.8 | 2.88 ± 1.56 | 139 ± 98.4 | 6.62 ± 4.69 | NE | 4.97 ± 2.32 |
| Hexanal | 91.9 ± 29.7 | 4.37 ± 1.41 | 65.5 ± 60.4 | 3.12 ± 2.88 | 1.81 ± 0.33 | 9.09 ± 6.25 |
| Octanal | 126 ± 17.5 | 5.98 ± 0.83 | 112 ± 44.1 | 5.31 ± 2.10 | 1.19 ± 0.98 | NE |
| Nonanal | 153 ± 60.0 | 7.27 ± 2.86 | 160 ± 54.2 | 7.63 ± 2.58 | NE | 13.5 ± 7.09 |
| Benzaldehyde | 210 ± 65.5 | 10.0 ± 3.12 | 826 ± 764 | 39.4 ± 36.4 | 5.84 ± 4.71 | 10.0 ± 4.19 |
| Acetone | 44247 ± 9971 | 2107 ± 475 | 58076 ± 2277 | 2766 ± 108 | -5.88 ± 2.92 | 41.9 ± 9.12 |
| 2-Butanone | 14804 ± 2830 | 705 ± 135 | 9916 ± 1313 | 472 ± 62.5 | 19.2 ± 0.86 | 33.1 ± 7.28 |
| 2-Pentanone | 6191 ± 2673 | 295 ± 127 | 3389 ± 677 | 161 ± 32.2 | 1.78 ± 0.92 | NE |
| 2-Methyl-3-pentanone | 343 ± 45.5 | 16.3 ± 2.17 | 259 ± 21.2 | 12.4 ± 1.01 | NE | NE |
| 2-Hexanone | 197 ± 54.9 | 9.36 ± 2.62 | 52.0 ± 12.8 | 2.48 ± 0.61 | -3.52 ± 2.82 | NE |
| 5-Methyl-2-hexanone | 450 ± 201 | 21.4 ± 9.59 | 351 ± 110 | 16.7 ± 5.24 | NE | 64.5 ± 17.4 |
| 2-Heptanone | 185 ± 19.7 | 8.79 ± 0.94 | 69.7 ± 11.2 | 3.32 ± 0.53 | 2.45 ± 0.99 | 3.16 ± 2.99 |
| 3-Heptanone | -1614 ± 182 | -76.8 ± 8.66 | -593 ± 491 | -28.3 ± 23.4 | -18.5 ± 4.96 | 99.0 ± 26.3 |
| 6-Methyl-5-hepten-2-one | 138 ± 20.7 | 6.57 ± 0.99 | 110 ± 75.2 | 5.26 ± 3.58 | 2.80 ± 0.79 | 1.99 ± 1.31 |
| 2-Octanone | 108 ± 3.11 | 5.16 ± 0.15 | 99.5 ± 0.65 | 4.74 ± 0.03 | 1.00 ± 0.88 | ND |
| 3-Octanone | 132 ± 22.1 | 6.30 ± 1.05 | 46.1 ± 2.34 | 2.19 ± 0.11 | 0.62 ± 0.17 | 0.56 ± 0.36 |
| Acetophenone | 398 ± 87.9 | 18.9 ± 4.18 | 2402 ± 177 | 114 ± 8.44 | 7.70 ± 4.57 | 4.33 ± 3.82 |
| 2-Methyl furan | 335 ± 41.8 | 16.0 ± 1.99 | 281 ± 43.2 | 13.4 ± 2.06 | NE | NE |
| 3-Methyl furan | 371 ± 56.5 | 17.7 ± 2.69 | 283 ± 46.5 | 13.5 ± 2.22 | NE | NE |
| 2-Ethyl furan | 119 ± 13.8 | 5.64 ± 0.66 | 107 ± 17.5 | 5.08 ± 0.83 | NE | NE |
| Hexyl acetate | 103 ± 36.8 | 4.91 ± 1.75 | 119 ± 47.3 | 5.66 ± 2.25 | 7.51 ± 1.68 | NE |
| Methyl butyrate | 34.6 ± 19.3 | 1.65 ± 0.92 | 104 ± 20.3 | 4.95 ± 0.97 | NE | NE |
| Ethyl butyrate | 8.94 ± 4.59 | 0.43 ± 0.22 | 96.4 ± 27.3 | 4.59 ± 1.30 | NE | NE |
| 1-Methylethyl butyrate | 18.2 ± 8.29 | 0.87 ± 0.39 | 348 ± 61.3 | 16.6 ± 2.92 | NE | 52.9 ± 25.5 |
| Butyl butyrate | 79.4 ± 50.4 | 3.78 ± 2.40 | 204 ± 137 | 9.72 ± 6.50 | NE | NE |
| Dimethyl sulfide | 54.0 ± 13.3 | 2.57 ± 0.63 | 86.7 ± 12.8 | 4.13 ± 0.62 | NE | NE |
| Carbon disulfide | 41.8 ± 6.00 | 1.99 ± 0.29 | 171 ± 9.42 | 8.13 ± 0.45 | 4.26 ± 2.63 | 0.41 ± 0.17 |
| Dimethyl disulfide | 4.90 ± 2.67 | 0.23 ± 0.13 | 1.33 ± 0.55 | 0.06 ± 0.03 | NE | NE |
| Dimethyl trisulfide | 8.91 ± 3.55 | 0.42 ± 0.17 | 0.77 ± 0.22 | 0.04 ± 0.01 | NE | NE |
| Chloromethane | 25.3 ± 3.78 | 1.21 ± 0.18 | 41.4 ± 5.26 | 1.97 ± 0.25 | 1.22 ± 0.66 | 0.92 ± 0.37 |
| Total VOCs | 131508 ± 28283 | 6262 ± 1347 | 98648 ± 16254 | 4698 ± 774 | 558 ± 235 | 461 ± 141 |

Values presented are mean with standard error and calculated on the dry mass of straw-soil mixture in test groups and soil alone in control groups unless otherwise noted. Values in italics are based on the dry mass of the straw alone. Negative values denoted the uptake of VOCs. NE: not emitted.

and non-flooded test treatments, respectively. It was followed by toluene and 2-butanone, accounting for 28.0% and 11.3% in the flooded test treatment and 8.6% and 10.1% in the non-flooded test treatment, respectively. However, benzene, ethylbenzene and xylene isomers as common accompaniments of

toluene (Misztal et al., 2015) were not emitted from the returned straw in the two test treatments. The predominance of OVOCs was consistent with their identification as major contributors to VOC emissions during the degradation of other plant litters (Warneke et al., 1999; Gray et al., 2010), while the

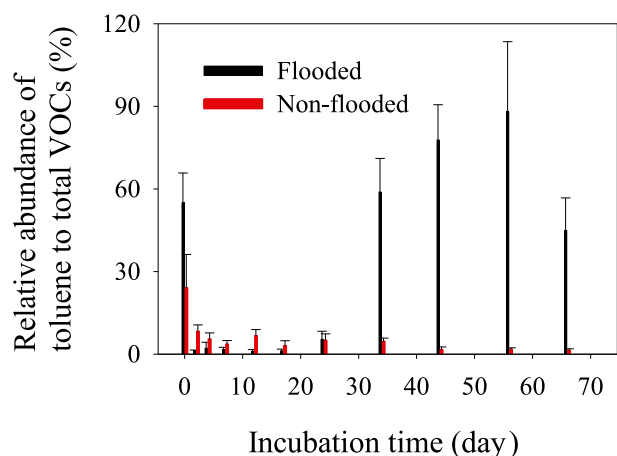


Fig. 1. – Abundance of toluene relative to total VOCs from the returned wheat straw in the two test groups during the incubation. The data were calculated with the emission rates of toluene and VOCs.

disappearance of similar alkylbenzenes conformed with their absence during the decomposition of other plant residues (Isidorov et al., 2003; Fedele et al., 2007; Gray et al., 2010; Ramirez et al., 2010). However, the dominance of toluene was uncommon compared to previous studies, although toluene has been identified to be common compounds and shared less than 5% or even 1% of the total VOCs released from many plant litters such as Scots pine, spruce, oak, red maple, aspen, green ash, eucalyptus, azalea, star thistle, miscanthus and quack grass (Isidorov et al., 2003; Fedele et al., 2007; Gray et al., 2010; Ramirez et al., 2010). The obvious disagreements in toluene emissions were largely attributed to the differences between litter types as well as incubation conditions elaborated in Section 2.3.

Toluene also had variable amounts relative to those of the total VOCs from the returned straw during the whole process in the two test groups (Fig. 1). The ratios of toluene to total VOCs were very high and accounted for 55.0% and 24.0% at the beginning under flooded and non-flooded conditions, respectively, and decreased drastically in the early 2 days and then became very low and steady until 24 days under the two moisture conditions. After 24 days, the proportion increased with incubation time and peaked at day 56 (88.1%) under flooded condition, while that was still steady under non-flooded condition.

It's also worth noting that toluene concentrations in the outgoing air were equal to those in the incoming air of the dynamic chamber in both the two control groups, that is, toluene was not released from soils alone during the 66-day incubation (Table 1). The result indicated that the incorporated straw was a source of toluene. Yet, Zhang et al. (2018) found toluene emissions were obviously predominant and accounted for 10.1% of the total NMHC emissions from soil with straw removal, but decreased 45.7% after straw incorporation in a maize cropping system under unflooded condition, implying that the agricultural soil was a source of toluene, whereas the amended straw was a sink. This obvious discrepancy might be owing to the strong differences in environmental

conditions. On one hand the present study was performed under controlled conditions without living plant, whereas Zhang et al. (2018) conducted their field experiment in a maize cropping system. Previous study documented that plant roots could synthesise and release a large number of VOCs in the rhizosphere and diffuse at various distances from the source (Delory et al., 2016), and a few studies did measure toluene emissions from maize plants (Bachy et al., 2016; Graus et al., 2013). This might lead to the release of toluene from soil with straw removal in the maize cropping field (Zhang et al., 2018). On the other hand in the present study toluene emissions were determined just after the straws returned in soil, while that was measured after the crop residues amended in soil for approximately seven months by Zhang et al. (2018). As mentioned in Section 2.2 in this study, toluene was only released in the early stage of the straw decay process under unflooded condition, and organic inputs could reduced VOCs emissions even less than the unamend control plots in agrosystems (Potard et al., 2017). This might cause the reduce of toluene emissions from test group with straw incorporation compared to control group with straw removal in a maize cropping system (Zhang et al., 2018). These together suggested that the effect of straw return on toluene emissions might be quite dissimilar under different experimental conditions. More studies are needed to accurately estimate the role of straw return on toluene emissions and fully understand its mechanism.

2.2. Emission rates of toluene

As presented in Fig. 2, the emission rates of toluene were relatively high at day 0, and decreased sharply with time to be very low in the first 2 days and then steady until 24 days in the two test groups. This finding suggested that during the first 2 days in the two test groups, toluene was mainly derived from primary volatilization of the inherited pool in crop straw. As previously reported by Misztal et al. (2011), a broad array of aromatic compounds including toluene are formed through different metabolic pathways in living plants, and can be emitted transiently upon cell wounding. Crop straw, as a pool of toluene, was cut before incubation and wet at the beginning of the experiment, making these compounds unable to be locked in clumps, but instead volatilize rapidly due to the increase of surface area and the replacement of compound molecules with moisture in the crop residues (Warneke et al. 1999). Quiet similarly, Fedele et al. (2007) found that toluene emissions from fresh leaf mulch and wood chips of *Grevillea robusta* (Australian Silky Oak) were high during the first hour but below detection after 24 hr.

After 24 days, the emission rates were very low even to be zero until the end of the experiment under non-flooded condition. Under flooded condition, the emission rates increased to form one “peak emission window” between days 24–56, and then decreased until leveling off and was close to zero after 56 days. The results indicated that toluene would be secondarily formed during the incubation rather than inherited under flooded condition, probably due to the microbial activity described in detail in Section 2.4. As reported by Richards and Sandau (2018), a high ratio of toluene to the sum of benzene, toluene, ethylbenzene, and xylenes (BTEX) (> 0.7) is indica-

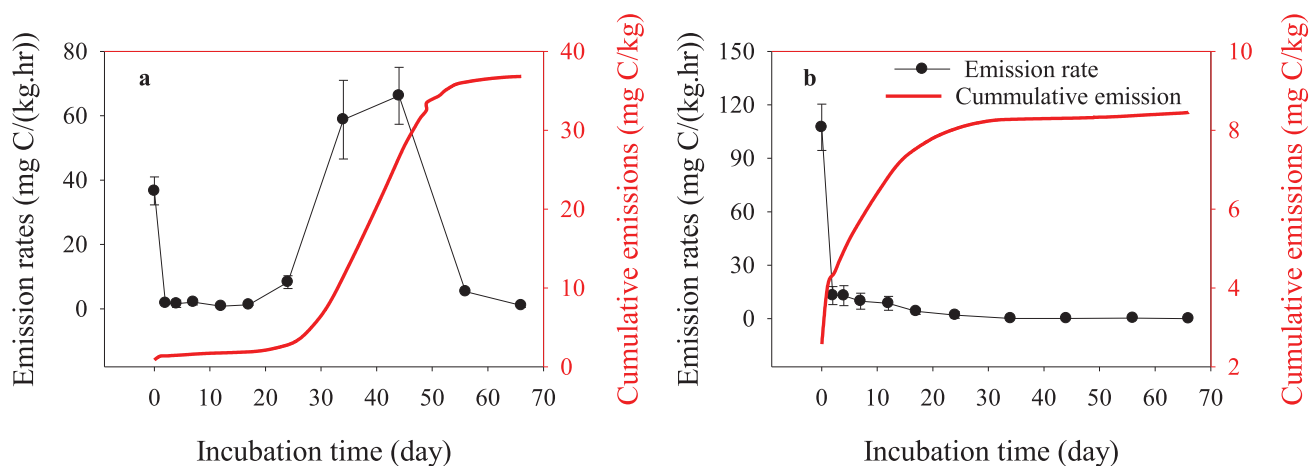


Fig. 2. – Emission rates and cumulative emissions of toluene from the returned wheat straw in the two test groups under (a) flooded and (b) non-flooded conditions, respectively.

tive of a biogenic origin rather than a petrogenic origin of toluene. Since benzene, ethylbenzene, and xylenes were not determined in the gas released from the returned straw in the two test treatments, the ratios of toluene to the sum of BTEX for samples in this study were always 1.0, implying its biogenic source. Quiet similar, Allen et al. (1997) also reported the majority of the aromatic compounds, alkanes and alkenes were produced in the late stage of the domestic waste degradation processes, probably from microbial degradation of organic matters. Actually, the emission profile of toluene in the study was in agreement with that of many C₂-C₅ NMHCs from the returned straw in our published data (Wang et al., 2015), with the second “peak emission window” at day 24-56, probably secondarily produced.

2.3. Emission masses of toluene

The mean mass of toluene emissions from the returned straw reached 36.8 and 8.45 mg C/kg over the entire process under flooded and non-flooded conditions, respectively. In other words, the emission mass of toluene from the returned straw under flooded condition was approximately 3 times higher than that under non-flooded condition. Over 90% of the emissions occurred between days 24-56, with over 55% emitted between days 34-44 under flooded condition, and probably secondarily formed. Under non-flooded condition, over 90% of the emissions occurred in the first 17 days, with over 50% released in the first 2 days under non-flooded condition, and probably inherited (Fig. 2). These results indicated that the emissions of toluene from the returned straw under flooded condition were greater than that under non-flooded condition, and primarily from secondary formation. This can be explained by the fact that biogenic toluene prefer to be produced during the microbiologic degradation of organic matters under anaerobic condition rather than aerobic condition (Richards and Sandau, 2018). Many previous studies have also observed an abundance of toluene release during the decomposition of organic matters in anoxic environmental matrices. For example, Jüttner and Henatsch (1986) found that appre-

ciable amounts of toluene was biogenically produced in the anoxic hypolimnion in a stratified lake, and that toluene concentrations increased with the decrease of oxygen concentrations in the depth profile. Mrowiec et al. (2005) observed that toluene was formed under anaerobic digestion of sewage sludge within waste treatment plants, with the concentration ranging from 0.2 to 42 mg/L. Toluene was also transiently determined in chloride-contaminated groundwater at high concentrations after a fermentable substrate (agricultural feed grade cane molasses) was injected into the subsurface to provide electron donors for reductive dechlorination by anaerobic bacteria (Moe et al., 2018).

Toluene emissions have been quantified from other plant litters including 3 grass species, 4 evergreen species and 7 deciduous species incubated with the water holding capacity (WHC) of 80%, ranging from 0.58 to 358, and 0.76 to 221 mg C/kg during the biotic and abiotic decomposition, respectively (Gray et al., 2010) (Table 2). Toluene emissions from wheat straw under flooded condition in the present study were comparable to that from the litters of two pine species, and approximately one order of magnitude lower than that from the litters of *Eucalyptus* sp., but 1-2 orders of magnitude higher than that from the litters of the left plant types during both the biotic and abiotic decomposition (Table 2). Under non-flooded condition, toluene emissions from wheat straw in the present study were 1-2 orders of magnitude lower than that from the litters of two pine species and *Eucalyptus* sp., but 2-13 times higher than that from the litters of the left plant types during both the biotic and abiotic decomposition (Table 2). This difference might be a consequence of the variation of toluene emissions with litter types as well as incubation conditions (Gray et al., 2010). It is worth noting that the toluene emissions from wheat straw amended in the soil in this study were about one order of magnitude lower than those from straw burning (205-270 mg C/kg) (Stockwell et al., 2014, 2016), indicating straw return can reduce toluene emissions in comparison to straw burning.

To further assess the significance of toluene emissions from returned crop straw for the global budgets, we perform a

Table 2. – Reported toluene emission mass from different plant litter species during the decomposition.

| Plant species | Degradation condition | Emission mass (mg C/kg) | References |
|---------------------------------|-------------------------------------|-------------------------|-------------------|
| <i>Centaurea maculosa</i> | Biotic, the WHC of 80% | 1.09 | Gray et al., 2010 |
| | Abiotic, the WHC of 80% | 1.34 | |
| <i>Rhododendron maximum</i> | Biotic, the WHC of 80% | 1.85 | |
| | Abiotic, the WHC of 80% | 1.34 | |
| <i>Quercus macrocarpa</i> | Biotic, the WHC of 80% | 1.60 | |
| | Abiotic, the WHC of 80% | 1.18 | |
| <i>Quercus rubra</i> | Biotic, the WHC of 80% | 1.93 | |
| | Abiotic, the WHC of 80% | 1.85 | |
| <i>Eucalyptus species (sp.)</i> | Biotic, the WHC of 80% | 358 | |
| | Abiotic, the WHC of 80% | 221 | |
| <i>Fraxinus pennsylvanica</i> | Biotic, the WHC of 80% | 0.59 | |
| | Abiotic, the WHC of 80% | 1.43 | |
| <i>Pinus contorta</i> | Biotic, the WHC of 80% | 42.5 | |
| | Abiotic, the WHC of 80% | 40.4 | |
| <i>Pinus ponderosa</i> | Biotic, the WHC of 80% | 85.0 | |
| | Abiotic, the WHC of 80% | 53.3 | |
| <i>Miscanthus sp.</i> | Biotic, the WHC of 80% | 0.59 | |
| | Abiotic, the WHC of 80% | 0.84 | |
| <i>Thinopyrum intermedium</i> | Biotic, the WHC of 80% | 0.76 | |
| | Abiotic, the WHC of 80% | 1.26 | |
| <i>Populus deltoides</i> | Biotic, the WHC of 80% | 2.77 | |
| | Abiotic, the WHC of 80% | 0.76 | |
| <i>Populus tremuloides</i> | Biotic, the WHC of 80% | 2.52 | |
| | Abiotic, the WHC of 80% | 1.01 | |
| <i>Triticum aestivum</i> | Biotic, the water depth of 8 ± 2 cm | 36.8 | This study |
| | Biotic, the WHC of 80% | 8.45 | |

WHC: water holding capacity.

simple estimate by assuming that dry crop residue production reaches approximately 2.9×10^9 ton/year in the world (FAO, 2020) and that 70% of these crop residues are returned to the soils as organic fertilizer (Bian et al., 2018) causing emission rates of toluene from crop straw in this study (8.45–36.8 mg C/kg), the global toluene emissions from straw return would be roughly 0.015–0.066 Tg C/year, accounting for approximately 1%–20% of that from biogenic sources (0.32–1.37 Tg C/year) (Sindelarova et al., 2014; Mísztal et al., 2015; Cabrera-Perez et al., 2016; Henrot et al., 2017). Since this estimation is calculated using optimal emission data at room temperature under two moisture conditions in a lab, ignoring the variation of degradation conditions, and crop straw types, it is not conclusive evidence. Further research should be conducted on toluene emission characteristics from different straw types under field conditions.

2.4. Relations of toluene emissions to soil microorganisms

Microorganisms play critical roles in soil VOCs emissions, including toluene (<http://bioinformatics.charite.de/mvoc/>) (Lemfack et al., 2014). As presented in Table S1, the average microbial respiration, biomass C, and population in straw-soil mixtures under flooded condition were obviously lower than those under non-flooded condition. Correlations between the emission rates of toluene (dependent variables) and the abundance of microbial biomass C, respiration rate (CO₂ flux), and population (independent variables) are presented in Fig. 3. Considering that toluene emissions were related with the inherent constituents of straw rather than the soil mi-

croorganisms at day 0 in the two test treatments and that the abundance of microbial biomass C, respiration rate (CO₂ flux), and population was not measured at day 66 in the test group under unflooded condition, the correlation analysis excluded the data at day 0 in the two test groups and at day 66 under unflooded condition in the present study. A significantly positive correlation was found between toluene emission rate and microbial biomass C under flooded condition. Negative associations were found for toluene emission rate with bacteria and fungus number, microbial biomass C, and CO₂ flux under non-flooded condition ($p < 0.05$). These results indicated that toluene may be mainly produced by microorganisms in straw-soil mixture under flooded condition, but primarily consumed by microbes under non-flooded condition. Previous studies have also found that a positive correlation can occur through the production of VOCs from microbes, while a negative correlation may result if the microorganisms consume VOCs from decomposing biowaste (Ramirez et al., 2010). This can be explained by the fact that toluene can be generated from the anaerobic microbial degradation of phenylalanine or terpene under anaerobic or anoxic conditions (Jüttner and Hentsch, 1986; Richards and Sandau, 2018). Many bacteria and fungus were reported to produce toluene such as *Burkholderia*, *Carnobacterium*, *Clostridium*, *Paenibacillus*, *Pseudomonas*, *Serratia*, *Tolurmonas*, *Antrodia*, *Coniophora*, *Pinus*, *Serpula*, *Tuber* (<http://bioinformatics.charite.de/mvoc/>) (Lemfack et al., 2014), and phenylacetate decarboxylase (PhdB), a glycol radical enzyme, and its cognate activating enzyme (PhdA), a radical S-adenosylmethionine enzyme were discovered from two distinct anoxic, toluene-producing microbial communities

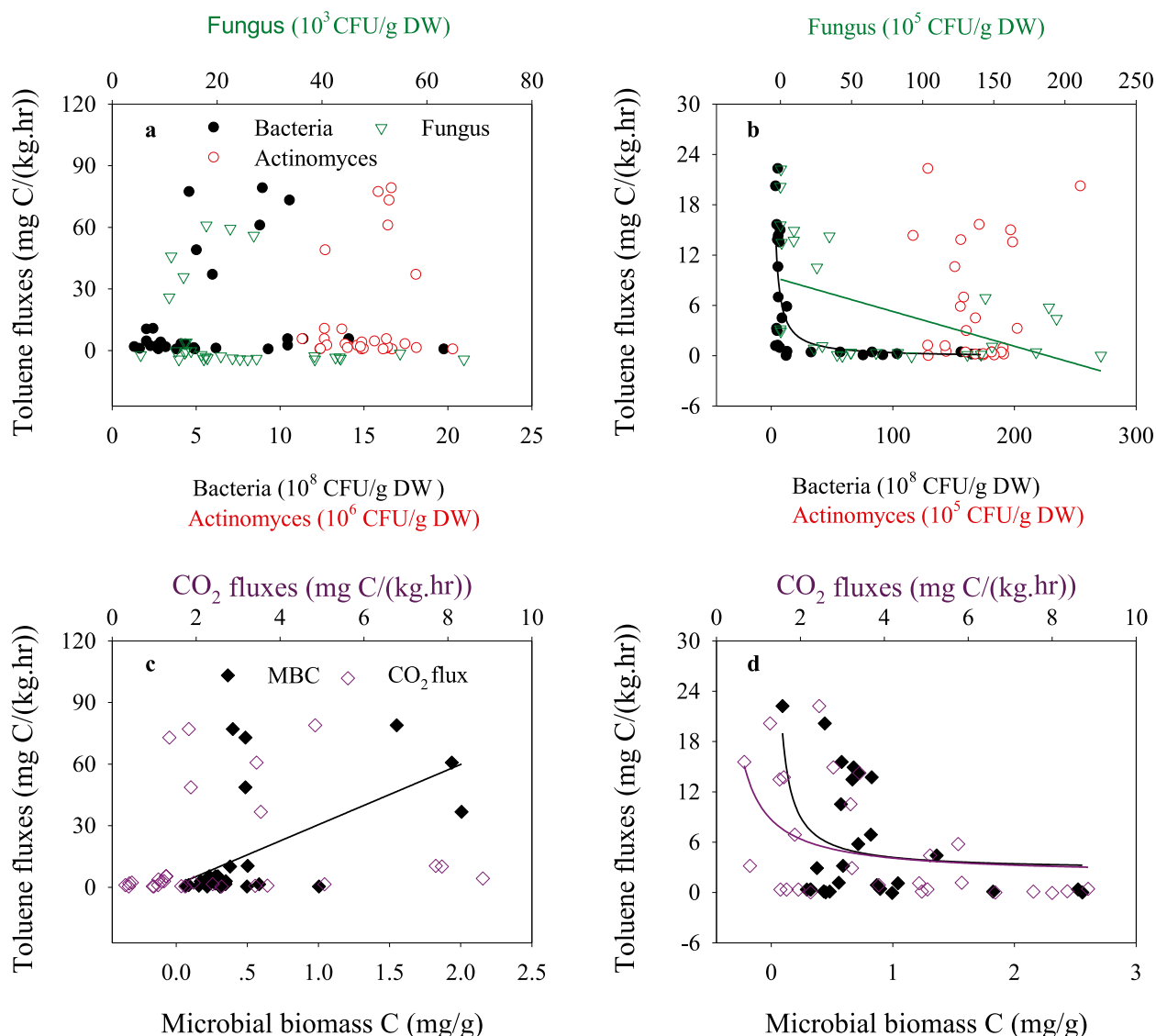


Fig. 3. – grCorrelation of toluene emissions with microbial population, respiration rate and biomass C in the test groups under flooded (a and c, $n = 30$) and non-flooded (b and d, $n = 27$) conditions, respectively. The regression equation for toluene emissions correlated with microbial biomass C under flooded condition is: $y = 29.3x + 1.16$ ($R = 0.57$, $p < 0.01$). The regression equations for toluene emissions related to bacteria and fungus numbers, microbial biomass C and respiration rate (CO_2 fluxes) under non-flooded conditions are $y = 54.7/x - 0.19$ ($R = 0.62$, $p < 0.01$), $y = -0.05x + 9.10$ ($R = 0.49$, $p < 0.01$), $y = 1.53/x + 2.66$ ($R = 0.41$, $p < 0.05$) and $y = 8.70/x + 2.03$ ($R = 0.42$, $p < 0.05$), respectively. CFU: colony forming unit; DW: dry weight.

(Beller et al., 2018). On the other hand, toluene can be also biodegradable by anaerobic microorganism with nitrate, arsenate, Mn (IV), Fe (III), humic substances, sulfate, and organic acids as terminal electron acceptors (Weelink et al., 2010) as well as aerobic microbe such as *Mycobacterium cosmeticum* (Zhang et al., 2013), *Pseudomonas plecoglossicida* (Li et al., 2017) and so on. Since abiotic sources of toluene are equally important to biotic sources during the degradation of plant residues (Gray et al., 2010), it is not enough to describe causal relationship between the emissions of toluene and microorganisms. We should also conduct experiment in the further study to observe the emissions of toluene only from microbial activity as well as to determine the proportional contribution

of straw, soil and microorganism to the emissions of toluene, respectively.

3. Conclusions

This manuscript reports on a laboratory study quantifying toluene emissions from wheat straw returned in agricultural soil under flooded and non-flooded conditions, respectively. We found that toluene emissions were observed only when wheat straw was added into soil and did not occur in controls without straw. Toluene dominated in released VOCs from the returned straw, accounting for 28.0% and 8.6% of total VOCs

under flooded and non-flooded conditions, respectively. The emissions of toluene under flooded condition were approximately 3 times higher than the corresponding value under non-flooded condition, respectively. Under flooded conditions, an initial period of high emissions was observed, followed by a second period of high emissions between 24 and 56 days. Under non-flooded condition, emission rates were high only during the first days and did decrease thereafter. The emission masses of toluene from the returned straw during days 24–56, probably secondarily formed, were significantly higher than those in the first 24 days, probably inherited in the flooded test group. These results together indicated that substantial toluene could be generated during the degradation of straw amended in soils, particularly under flooded condition, and primarily derived from the secondary product. Another finding is that toluene emission rates were significantly positively correlated with microbial biomass C under flooded condition, but negatively associated with bacteria and fungus number, microbial biomass C, and CO₂ flux under non-flooded condition, implying that microorganisms might play important roles in toluene emissions from the amended wheat residues. A rough estimate showed that global crop straw return could contribute to about 1%–20% of biogenic toluene budgets, and it should be not neglected. So crop straw returned would be biogenic source of atmospheric toluene, although the magnitude of the emission strength of these sources needs further investigation. The results could provide useful information to understand toluene biogenic sources.

Acknowledgments

Financial supports from [Natural Science Foundation of China](#) (Nos. [41273095](#) and [40203011](#)), [Natural Science Foundation of Anhui Province](#) (No. [2008085MD111](#)) and the University Synergy Innovation Program of Anhui Province (No. [GXXT-2020-075](#)) are gratefully acknowledged. Thanks, are also given to Ran Wang, Zhe Wang, Yujie Zhang, Gang Yang, Sujun Lv, Zhou Zhang, and Yanli Zhang for their help with this research.

Appendix A Supplementary data

Supplementary material associated with this article can be found in the online version at [doi:10.1016/j.jes.2021.08.050](https://doi.org/10.1016/j.jes.2021.08.050).

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