We appreciate the constructive comments of the reviewer on our manuscript. We have carefully responded to all comments accordingly. The revisions are described in details below.

Response to Reviewer #2:

This paper discussed one of the insecticide such as NPM and its aqueous photochemistry could be a significant source of HONO and NOx especially when only compared to soil emissions. If this is true, the widely usage of insecticide could be another reason for the general discover of the presence of HONO even in the rural and remote areas. This study therefore make an interesting contribution to the community to bridge the argriculature insecticide (kind of emerging pollutants) and the atmospheric chemistry. I suggest publication after the authors to address my following comments.

General comments

As the authors mentioned, the kinetic study is performed for extremely high concentration level (- 50000 imu g L^-1}) which is several orders of magnitude higher than the environmental concentrations. Would the kinetics be different for the much lower concentrations? The authors may add some uncertainty discussions on this aspect according to possible theoretical approaches.

Response: As the reviewer suggested, we explored the kinetics of NPM at lower concentration (0.1 mg mL^{-1}), which is close to the limit of detection considering both NPM and reactive nitrogen species detection. As shown in Figure R6 below and in Figure S6, the kinetic data has shown a robust linear relationship between NOx and HONO production and light density at different NPM levels. The obtained results show that the rate constant (k) is faster at low NPM concentration compared to that of high NPM concentrations. It is important to note that, although our kinetic experiments are not capable of simulating concentrations under the environmental concentration, we selected a rationalization parameter scheme related to the environmental concentration of NPM (50 µg L^{-1}) and soluble iron (92.48 nmol L^{-1}, 0.025 mg L^{-1} in our study), in order to estimate the environmental NPM and iron concentration contributed to the formation of reactive nitrogen species which is representative to a certain level. In addition, the main scope of our study is to reveal that the light-induced degradation of NPM leads to enhanced production of HONO and NOx driven by secondary photochemistry between redox reaction of Fe^{3+}/Fe^{2+} and photoproduced ROS. We quantified the photochemical HONO and NOx formation through NPM photodegradation, and we suggest that this chemistry may represent a significant source of HONO and NOx in the regions where surface waters are polluted with NNs insecticides.

In the revised manuscript, we added the sentence "The kinetic data has shown that the rate constant (k) is faster at low NPM concentration compared to that of high NPM concentrations (Figure S6)."

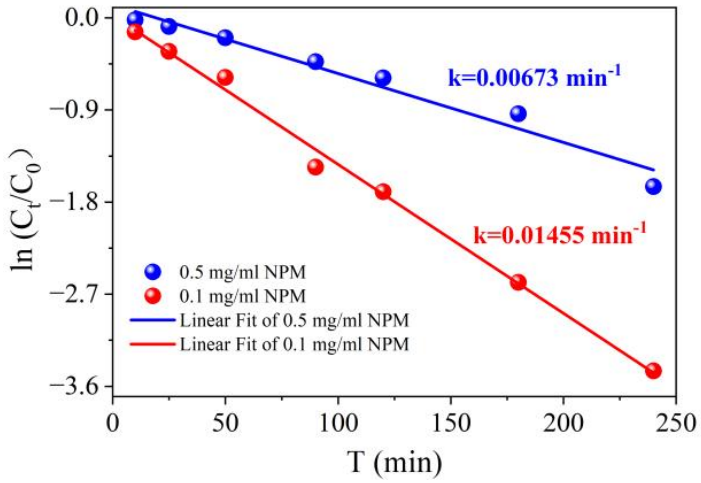

Figure R6. First-order rates at different NPM concentrations

Specific comments

1. HONO is indirectly measured as the difference between the NO_2 signal and the Na_2CO_3 tube. This could be subjected with some uncertainty. Other reactive nitrogen species might be included in this differential signal. The uncertainty discussions maybe added.

Response: NO, NO_2 and HONO concentrations were detected using a chemiluminescence NOx analyzer (42i, THERMO) with a molybdenum converter. Because HONO was detected by a quartz tube (25 cm length, 2.9 cm inner diameter) filled with Na_2CO_3 between the reactor and the analyzer was employed to remove HONO. The removal efficiency of HONO by the Na_2CO_3 tube reached 99% at the steady sate both in our study and previous work (Han et al., 2016). And the detection technique for HONO has been widely employed to measure the HONO concentration in many studies (Han et al., 2016; Yang et al., 2020). Meanwhile, it should be noted that NO_2 and NO are barely captured by the Na_2CO_3 tube as shown in the Figure R3. In order to validate the feasibility of the method, we also performed additional test experiment to confirm the indirectly determined HONO values by using Water-Based Long-Path Absorption Photometer (WLPAP, Beijing Zhichen Technology Co., Ltd, China) on-line connected with the reactor for real-time measurements of HONO, and the results agree well with the performed measurements by Na_2CO_3 tube (Figure R4).

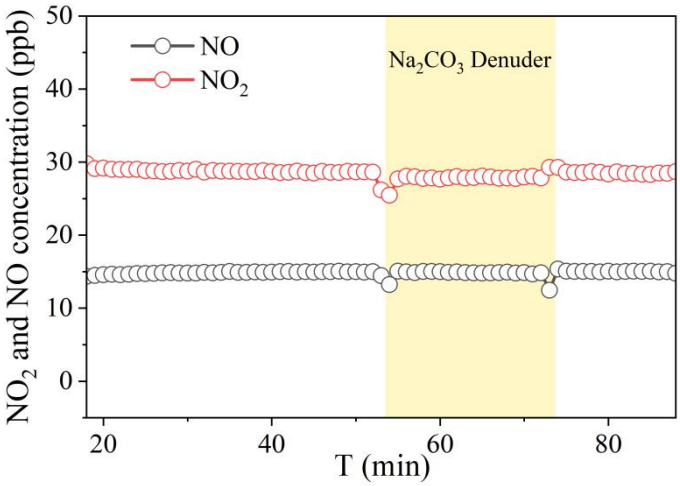

Figure R3. The adsorption of NO_2 and NO in the reactor by Na_2CO_3 tube

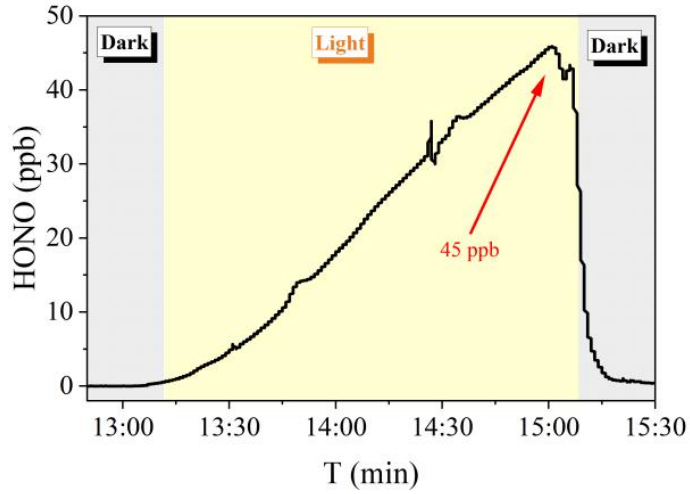

Figure R4. Typical HONO profile measured in real time by WLPAP analyzer upon irradiation of NPM. Conditions: Irradiation intensity of 169.4 W m^{-2} at 300< λ <400 nm, NPM concentration of 0.1 mg ml^{-1}, temperature of 298 K

2. Sect. 2.5, I have quickly checked the unit of the equation 3 and 4, I can end up with the unit of min^-1, but it is better converted to s^-1, the authors may further clarify it.

Response: Thank you for your suggestions and we apologize for the misunderstanding.

The photolysis frequencies (J-values, S^{-1}) of NPM to HONO and NOx were calculated by Eq.(3) and Eq.(4), respectively.

$$J_{NPM\rightarrow HONO} = \frac{QM_{NPM}\int_0^t C_t^{HONO}dt}{60\times10^{-3}N_A\times t\times(m_0+m_t)/2} \quad (3)$$

$$J_{NPM\rightarrow NOx} = \frac{QM_{NPM}\int_0^t C_t^{NOx}dt}{60\times10^{-3}N_A\times t\times(m_0+m_t)/2} \quad (4)$$

Where Q (mL min^{-1}) and M_{NPM} (g mol^{-1}) are the total flow gas rates in the reactor and the molar mass of NPM, respectively; t (min) is the irradiation time; Ct^{NOx} (molecules cm^{-3}) is the concentration of gaseous HONO or NOx formed by photolysis of NPM during the irradiation period; N_A is the Avogadro number; M_0 (mg) and M_t (mg) are the masses at the beginning and end of the NPM photolysis experiments.

The constant 1/60 in Eqs. 3 and 4 represents the conversion of min^{-1} to S^{-1}.

3. In the reference part, Wang Y et al., 2021 is duplicated.

Response: Thank you for noticing this. It is corrected.

References:

Han, C., Yang, W. J., Wu, Q. Q., Yang, H. and Xue, X. X.: Heterogeneous photochemical conversion of NO_2 to HONO on the humic acid surface under simulated sunlight. Environ. Sci. Technol. 2016, 50, 5017–5023.

Yang, W. J., Yuan, H., Han, C., Yang, H.and Xue, X. X.: Photochemical emissions of HONO, NO and NO from the soil surface under simulated sunlight, Atmospheric Environment. 2020, 234, 117596.