Responses to reviewer 2's comments

We appreciate your comments and contributions to improving this manuscript. We have resolved all issues and revised the manuscript accordingly. Please note: reviewers' comments are in black; our comments are in red and revised text in blue.

Reviewer Comments:

The manuscript is well written and easy to follow. The references list covers very well previous work. My main problem with the manuscript is the novelty. In my view much more work should have addressed sewer measurements and the challenges with such kind of measurements. The instrument and its operation are very similar to many previous works on PAS technology, which make descriptions similar to those in the manuscript. The real sewer measurements are only dealt with in lines 190 to 199. I find the title somewhat misleading. At least I expected much information and discussion related to sewer measurements. Prior to publication the authors should address the main novelty of their work. In addition, the authors should address the following specific comments/questions.

Point 1: L. 62-63: The authors' state that the gas molecules return to the ground state via non-radiative processes. What hinders them in returning by radiative processes?

Response 1: When the laser is incited into the photoacoustic cell, the photons of the excitation light source are absorbed by the gas molecules and lead to the transition of the molecular energy levels. Due to the instability of the excited state, the gas molecules will return to the ground state via non-radiative process or radiative process to return to the ground state. Non-radiative process plays an important role in the photoacoustic spectroscopy. Gas molecules return to the ground state through collision deexcitation (non-radiative process). In this process, heat energy is released, which increases the gas temperature in the local space, and the gas volume will also increase. By modulating the laser, the gas expands and contracts periodically, thus generating sound waves. In addition to non-radiation process, there is also radiation process, which mainly releases photons, corresponding to the fluorescence spectrum or phosphorescence spectrum, which has no contribution to the photoacoustic signal, so the radiation process is not considered in the photoacoustic spectroscopy.

Point 2: L. 90-94: Yes, DFB lasers are relative cheap in the communication wavelength range, however, in the described work an EDFA is added and thus the radiation source is not that cheap any more.

Response 2: As the reviewer mention, the EDFA used in the experiment is not cheap, but thanks to the development of optical fiber communication technology, the relevant technology of near-infrared band fiber amplifier has been fully developed, and its cost has also decreased significantly year by year. For example, according to our inquiry, the price of 1582nm band EDFA produced by Connet FIBER Optics Co., Ltd. has been reduced to less than 10,000 RMB, which still has a significant advantage over the cost of mid-infrared laser. Thanks for the reviewer's opinion, we will pay more attention to the cost in the subsequent product development process.

Point 3: L. 105: Why is 680 Torr an interesting pressure?

Response 3: As can be seen from Fig. 2(b), the photoacoustic signal is the highest under atmospheric pressure. In addition, from a practical point of view, it is more convenient to measure under atmospheric pressure (680 Torr), because there is no need to use a pressure controller under this condition.

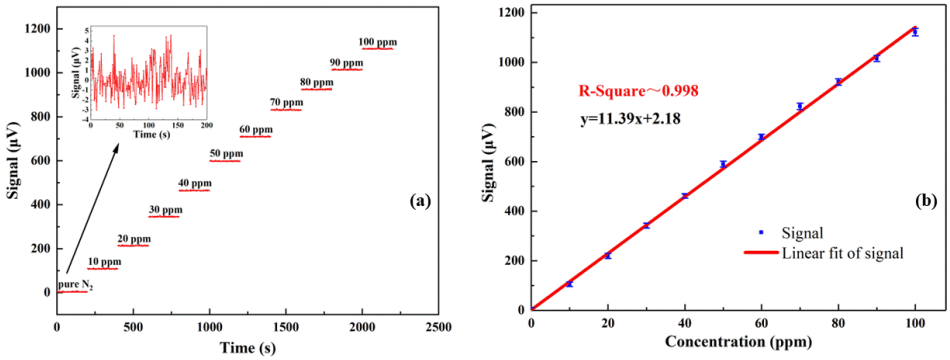
Point 4: L. 116-122 are rather trivial information. Same for L. 130-136.

Response 4: Thanks for the reviewer's comments. In order to avoid repetition, we have modified L. 130-133 of the manuscript:

"As a representative, the hydrogen sulfide PAS spectral scans obtained for the lowest (100 Torr) and the highest (680 Torr) pressure are shown in Figure 2(a). At 100 Torr, four spectral features can be identified, while the single absorption is obtained at 680 Torr as the atmospheric collisional broadening."

Point 5: Fig. 3B: Error bars are missing for the data points. These are needed in order to provide an overall uncertainty of the measurements.

Response 5: Fig. 3(b) has been modified in the manuscript. Thank you again for your comments.



Point 6: L. 180-183: Where these samples premixed or mixed on site? If the latter is the case, how were the mixing controlled?

Response 6: A gas blender was used to mixed the gases on site. The basic principle is to control the flow rate of different gases to change the concentration. The gas blender and its principle used in this experiment can be found in https://www.mcqinst.com/gas-mixer-for-life-science/.

Point 7: L. 183-186: The results are somewhat surprising. Although the mentioned molecules, except H_2S, are not excited at 6230.60 cm^{-1}, collisional relaxation effects should be expected, particular with the presence of the polar molecules NH_3 and CO. Can the authors explain this?

Response 7: This problem pointed out by the reviewer is one of the key concerns of our experimental research. In order to avoid gas cross interference, we conducted spectral line investigation in the early stage. As shown in Figure 1, the HITRAN database show that there is a 0.6 cm^{-1} shift between the absorption line of CO gas and the absorption line of H_2S target gas. For photoacoustic spectroscopy, this difference can be completely avoided by accurately controlling the laser wavelength. The NH_3 absorption line is close to the H_2S absorption line. Fortunately, the H_2S gas absorption line is more than ten times higher than NH_3, so the interaction between spectral lines is small. To verify the above analysis, we also carried out corresponding experimental research, and

the results are shown in Fig. 5. It should be pointed out that in special situations, such as when NH_3 concentration is much higher than H_2S, the measurement results will need to be corrected. We also supplemented relevant descriptions in L. 187-189:

"In addition, the measurement results need to be calibrated in special cases, such as when the concentration of ammonia is much higher than the hydrogen sulfide. But this situation hardly exists in reality."

As the reviewer said, the gas relaxation rate will affect the amplitude and phase of photoacoustic signals, and the gases with high relaxation rate, such as H_2O and SF_6, will generally improve the relaxation characteristics of the gases with low relaxation rate, such as CO and CH_4, thus affecting the measurement results of photoacoustic spectroscopy. It is well known that the molecular relaxation time τ should be much shorter than the modulation period in photoacoustic spectroscopy ($1/f$), i.e., $\tau << 1/f$. In the photoacoustic spectroscopy, the laser modulation frequency is consistent with the resonance frequency of the photoacoustic detect. For the photoacoustic cell used in this manuscript, the resonance frequency is 1779.8 Hz. Therefore, as long as the gas relaxation time is shorter than 0.562 ms, the influence of the relaxation rate on the photoacoustic signal can be basically excluded. This is obviously satisfactory for H_2S. From our previous research results, such as Ref. 2, even for QEPAS technology with modulation frequency up to 32 kHz, the influence of the gases in the atmosphere, such as CO, NH_3, H_2O, etc., on the relaxation rate of H_2S can be ignored. Further, our experimental results also verify this conclusion as shown in Figure 5. To illustrate this point, we added a description in L. 185-187:

"Furthermore, this result shows that the influence of common gases in the sewer on the relaxation rate of H_2S can also be ignored."

Point 8: Ammonia is a highly sticky molecule. It could very well happen that it sticks to the collection bag as well as to the walls of the PAS cell. The 81.5 ppm should be quoted with an uncertainty, otherwise it does provide a definitive conclusion.

Response 8: As the reviewer said, ammonia has a good adhesion, but for low concentration of ammonia, the dynamic equilibrium can be achieved within a short time and a small volume. To ensure the accuracy of the experimental results, we will flush the gas circuit with pure nitrogen before each measurement, and then use the target gas to continuously and dynamically inflate for a period of time to ensure the correctness of the measurement results.

Point 9: What happens to the gas mixture during transportation?

Response 9: As mentioned in point 8, the adhesion of ammonia needs to be taken into consideration. Therefore, sample gas is used to wash the sampling bag during each sampling process, and sample gas is collected and transported sealed after ammonia adsorption and desorption achieve a dynamic balance. In addition, the measurement of sewer gas can be carried out by air collection bag sampling, which has no effect on the experimental results. This method is also used in other manuscript "Occurrence of chlorinated volatile organic compounds (VOCs) in a sanitary sewer system: Implications for assessing vapor intrusion alternative pathways", doi:10.1016/j.scitotenv.2017.10.205 .