Supplementary information

**The** **soil** **displacement measurement of mercury emission flux of the** **sewage irrigation farmlands in northern China**

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***S 2.1. Design of soil displacement measurement***

The specific conditions are as follows: first, in early June 2016, summer maize was planted in the experimental plots with plant spacing of 20 cm and row spacing of 30 cm. Subsequently, winter wheat was sown with plant spacing of 0.6 cm and row spacing of 30 cm in the experimental plots after maize harvest and plots rotation tillage in early October of the same year. Finally, after the winter wheat harvest in early June 2017, the next maize was grown in the same way as in 2016.

***S 2.2. Measurement of soil-air TGM exchange flux***

Current international methods for measuring soil-air TGM exchange flux are dynamic flux chamber method (DFC) and micrometeorological method(Feng et al., 2011). However, the micrometeorological method is applicable to the large area of uniform underlying surface, and it is required that the atmospheric conditions are constant during the observation period(Feng et al., 2011). So, it is not suitable for the observation with large time spans and large changes in meteorological factors. Moreover, the data measured by the micrometeorological method are mostly soil-air-crop composite TGM fluxes of farmland ecosystems rather than soil-air TGM exchange fluxes. Although the DFC method has some limitations, it has the advantage of simplicity and practicability. The coverage of the chamber is usually less than 1 m2, which is suitable for the observation of soil-air TGM exchange flux under the crop canopy in field plots. The DFC method has been used by many research groups at home and abroad, Such as Gustin, Lindberg and Carpi groups in USA (Briggs et al., 2014; Carpi et al., 2014; Eckley et al., 2011; Eckley et al., 2016; Miller et al., 2011), Poissant, Schroeder and St. Louis groups in Canada (Poissant et al., 2004; Schroeder et al., 2005), Ebinghaus, Ferrara, Horvat and Lindqvist groups in Europe (Ebinghaus et al., 2011; Eckley et al., 2015; Ferrara et al., 1998; Kock et al., 2005; Xiao et al., 1991), Kim group in Korea (Eckley et al., 2016), Feng Xinbin, Wang Dingyong, Duan Lei， Zhang Xiaoshan groups (Du, 2014; Fu et al., 2012; Wang et al., 2016; Zhou et al., 2017) and so on, to measure the TGM exchange flux between the various surface interface of terrestrial ecosystems and the atmosphere. Moreover, it is different from other terrestrial ecosystems that farmland soil is mixed more evenly in topsoil layer due to long-term and frequent cultivation. The measured data of DFC method are more representative and reliable than other terrestrial ecosystems. Due to limited field test conditions, the automatic mercury measurement system, which requires large amounts of electrical energy, has not been adopted. In addition, although the automatic sampling system can improve the time resolution of observation, it is necessary to measure the soil-air TGM exchange rate of the five test plots in turn, which makes the observation data in different plots have a certain time difference and may reduce the comparability of the data.

This study was carried out between August and next July from 2016 to 2017, lasting 225 days. Measurements of soil-air TGM flux and meteorological parameters started at early August, 2016. Subsequently, after the maize harvested and the plots plough, the measurement of TGM flux during winter wheat lasted from October 10 to June 10 in the following year. After the harvest of winter wheat, an experiment was added to observe the TGM exchange flux during seeding season of the maize until July 10, 2017.

The summer maize growth period was divided into five stages: tillage-sowing (June 11~20, 2017), seedling (June 21~28, 2017), early jointing (June 29~July 10, 2017), jointing-heading (August 6~31, 2016) and milky-maturity (September 1~30, 2016); and the wheat growth period was consisted of six stages: tillage-sowing (October 1~13, 2016), seedling (October 14~November 5, 2016), overwintering (January 4~19, 2017), regreening (March 14~31, 2017), jointing(April 1~30, 2017) and heading-milky (May 1~June 10, 2017), basically modular in month (Fan et al., 2016; Ihsan et al., 2016; Luo et al., 2017). The flux data coverage was 81 % of maize growth and 58 % of wheat season. The reasons for the gaps mainly resulted from the operation time of Luancheng station-CAS, calibration, reference and power failures. In addition, the gaps in wheat period was concentrated in winter (late November, December and February), when vegetative growth extremely slowed and changes in environmental factors were not significant due to the harshness of the climate. Therefore, the observation period could well represent the duration of a full year period.

Our semi-cylindrical and quartz chamber was 10 cm high and 30 cm long with a footprint of 0.06 m2 (0.2m\*0.3m) and an internal volume of 4.71 L. In this observation, we used sets of improved DFCs to measure the *C*O and *C*i: one chamber was open-bottom to measure *C*O, and the other one was close-bottom by quartz plate to measure *C*i. Both of DFCs were placed under the canopy in the test plots under the normally growing crop canopy, and the sample soil was used to seal the open-bottom of the flux box in contact with the soil surface. A gold cartridge was connected to the outlet of the chamber to trap Hg at a sample flow rate of 0.036 m3 h-1. A soda lime drying tube made by Teflon was placed to remove moisture from the air and supplely filter large particles in the air. The soda lime was placed before every gold cartridge.

Several measures were taken to maintain high standard measurements. Quartz glass has many advantages as a construction material used in chambers for the determination of surface-air TGM flux measurement in both background and enrich soils (Ci et al., 2016a). In this study，every DFC was heated at 650 ℃ lasting more than 12 hours before the experiment. During the sampling process, the DFCs were cleaned once every week with ultrapure water and cleaned once more after each precipitation. All of the pipelines used to connect the DFCs, the gold cartridges, soda lime trap and integrating flow meters were made of Teflon. As a result, the blank flux values of the system were found to be very low (mean SD: 0.01~0.02 ng m-2 h-1) and were not significantly different throughout the entire study period. In addition, the difference could be ignored during calculating by using Eq. (1) in respect of using the open-bottom and close-bottom DFCs. Moreover, the DFCs were moved to another part of the test plot every day, in order to minimize the impact on soil physical and chemical properties.

Before and after the experiment, the collection efficiency, and parallelism of gold cartridges were measured. The collection efficiency of gold cartridges was determined by multiple measurements using gold cartridges in series in laboratory at a range of 1.0 to 30.0 ng m-3 of Hg concentration, the results showed that no breakthrough at the sample flow rate of 0.036 m-3 h-1 for 12 hours. And the recovery efficiency was between 97.8~102.3 %. It is stated that the gold cartridges used in this test met the test requirements. All the gold traps were tested by CVAFS detector (Brooks Rand III, US EPA, Method 1631, 1999) for mercury quantiﬁcation, using dual gold trap amalgamation procedure after every sampling (Ci et al., 2011; Ci et al., 2016b). The method detection limit was 0.03 ng m-3 and the precision was 3 ± 2 %. And the soda lime drying tubes were purified by Hg-free high purity argon gas for an hour before use.

**Table S captions**

**Table S 1**

Coefficient of correlation between soil-air TGM exchange flux and ambient-air TGMconcentration.

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Coefficient of correlation between soil-air TGM exchange flux and ambient-air TGM concentration.

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| --- | --- | --- |
|  |  | Ambient-air TGM |
|  |  | Maize season | Wheat season |
| Soil-air TGM exchange flux | TY | -0.24\*\* | -0.89\*\* |
| LC | -0.22\*\* | -0.89\*\* |
| TJ | -0.20\* | -0.84\*\* |
| SJZ | -0.16\* | -0.44\*\* |
| XA | -0.27\*\* | -0.32\*\* |

Note: \*\* means that the correlation was significant at 0.01 level (double tails), \* means that the correlation was significant at 0.05 level (double tails),

**Figure S captions**

**Fig. S 1.** Ambient-air TGM concentrations at Luancheng Station in four seasons and two harvest stages. The red lines are the mean concentrations of ambient-air TGM for each season and harvest stage.

**Fig. S 2.** Temporal variations of soil-air TGM exchange flux at Luancheng plot and environmental factors in maize-wheat rotation period.

**Fig. S 3.** Temporal variations of soil-air TGM exchange flux at Taiyuan plot and Tianjin plot in maize-wheat rotation period.

**Fig. S 4.** Temporal variations of soil-air TGM exchange flux at Shijiazhuang plot and Xi’an plot in maize-wheat rotation period.



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**Fig. S 4.** Temporal variations of soil-air TGM exchange flux at Shijiazhuang plot and Xi’an plot in maize-wheat rotation period.

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