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

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ABSTRACT
Mercury fate of sewage irrigation in farmlands deserves attention with increasing scarcity of freshwater resources for agriculture in the worldwide. Soil-air total gaseous mercury (TGM) fluxes from four-sewage and one-fresh water irrigated farmlands were determined simultaneously. During maize-wheat rotation, soil-air TGM flux showed patterns of both emission and deposition during different growth stages. It enhanced one-order of magnitude emission with increased Hg contamination from historical sewage irrigation. A linear response relationship of TGM fluxes with soil Hg concentration was found, which showed greater TGM emission potential comparing with those from forest and urban soils. However, the ratio of soil-air TGM flux in daytime to nighttime were 3.94 in maize-season and 3.41 in wheat-season, respectively, which were little related to the change in soil Hg concentration. Furthermore, soil temperature and moisture, ambient-air TGM concentration all effect TGM evasion from sewage-irrigated soils. The data presented here suggest that evasion of TGM from historical sewage irrigation farmlands with high Hg concentrations may be potential hotspots for Hg emission in atmosphere, and it was likely to underestimate Hg emissions from farmlands in existing emissions inventory. Additional regional-investigations and process-level researches are needed to better understand role of sewage irrigation farmlands in local-global Hg-biogeochemical-cycles.

Introduction
Mercury (Hg) is considered as a key global pollutant resulted from its persistence, bioaccumulation, and toxicity in the environment (Driscoll et al. 2013; Wang et al. 2016). Due to its special physical and chemical properties, Hg can be continuously transferred and transformed between different environmental interfaces, which means that Hg emitted from local areas will eventually affect the global ecosystem and harm the human health (Chen et al. 2019; Zhu et al. 2016). The terrestrial environment, which is reported as the largest Hg reservoir, plays a major role in the global Hg cycle (Obrist, Faïn, and Berger 2010; Pacyna et al. 2010). The annual amount of Hg released from soil to atmosphere is about 1700 ~ 3000t, accounting for approximately 1/3 of the total global Hg emissions (Selin 2014; UNEP 2013). In previous studies, researchers usually focused on the soil-air total gaseous mercury (TGM) exchange process in the background areas (Ci et al. 2016; Ericksen et al. 2006; Zhu et al. 2011). However, human activities (particularly mercury mining, amalgamation, sewage discharge, and waste dumping) have contaminated many land regions with Hg, and the total Hg (THg) concentration in these soils is usually significantly higher than those in the background areas (Li et al. 2009). With the further researches of global soil-air TGM exchange, an increasing number of scholars have stated that although the Hg contaminated sites are small in size, the TGM release rate from these soils to the air is usually several to thousand times higher than that from the background regions due to the high THg (Eckley et al. 2011; Wang et al. 2007).

Since the 1970s, with the increasing scarcity of freshwater resources and the increasing discharge of sewage, sewage irrigation has rapidly developed worldwide. The primary problem of sewage irrigation is that the heavy metal pollutants in sewage exceed the standard of the integrated wastewater discharge standard (Hg: 0.05 mg L⁻¹, GB8978-1996) (General Administration of Quality Supervision 1996), resulting in the pollution of soil-water-plant system. Soil contaminated by Hg has gradually been a universal global ecological environment issue over the same period (Yin, Gao, and Fan 2011; Zheng et al. 2016). Moreover, the distribution of Hg in farmland soils in sewage irrigation regions shows great spatial variability due to the complex surface environment and sources of sewage irrigation water (Yang et al. 2005). This leads to a huge difference in the soil-air TGM exchange flux in sewage irrigation farmlands (Lin
et al. 2010; O'Connor et al. 2019). The researches on soil Hg pollution in sewage irrigation areas mainly focus on soil environment, groundwater quality, crop physiology and food safety (Rothenberg et al. 2007; Wang et al. 2018; Xin and Li 2011). With the increasing understanding of hazards of sewage irrigation on farmland ecosystem, sewage irrigation has been gradually controlled in some countries (Xue 2012). However, due to the fact that heavy metals cannot be naturally degraded and difficult to be absorbed by plants, Hg pollution in farmland soils with sewage irrigation history has become a legacy problem after the cessation of sewage irrigation. Therefore, the study on the soil-air TGM exchange flux in historical sewage irrigation areas will significantly promote the understanding of regional and global Hg cycles.

China is not only the largest Hg emitter in Asia (Huang et al. 2017; Jiang, Shi, and Feng 2006) but also the country with the largest sewage irrigation area in the world (Li et al. 2014; Xu et al. 2018). The northern China, with a serious shortage of water resources, is the sewage irrigation concentrated area besides the main crop production region. The area of sewage irrigation in northern China once accounted for about 85% of the national sewage irrigation area (Fan et al. 2014; Rothenberg et al. 2007). Large sewage irrigation regions were mainly distributed in the suburbs of large and medium-sized cities in northern China in the past. The national general survey of soil contamination report shows that 19.4% of survey farmland soil points exceeded Level II requirements of the Soil Environmental Quality Standard (GB 15,618–2009); Hg is one of the major contaminants with excess ratio of 1.6% (Ministry of Ecology and Environment and Ministry of Natural Resources 2014). As a result, the Chinese government tightens norms for soil pollution legislation in an attempt to build a systematic management system which includes laws, action plans, regulations, risk control rules (control standards), and technical guidelines (Li et al., 2019). In addition, due to the severe shortage of water in the northern China, the Chinese government has reduced the quota for irrigation water use in farmlands (Fang et al. 2018), sewage irrigation was discontinued around 2000 in many provinces. However, as a potentially important source of TGM emissions, TGM emissions from soils there will affect Hg cycling at regional scales. Accordingly, this paper intended to observe the natural soil-air TGM exchange of farmland soil with different Hg polluted levels in typical regions with sewage irrigation history in northern China after sewage irrigation stopped by using the soil displacement method. And the characteristics and influencing factors were recognized. This study may help to improve the accuracy of the TGM emissions forecast list for contaminated sites and reduce the uncertainty of the assessment of the global biogeochemical cycle of Hg.

Materials and methods

Design of soil displacement measurement

Due to the wide distribution of the regions with sewage irrigation history in northern China and the large difference in latitude, the crop growth and meteorological conditions in each sewage irrigation region are inconsistent. In-situ measurement is not only difficult to achieve continuous multipoint observations, but the results will not be comparable due to different observation periods. Consequently, the soil-air TGM exchange fluxes of typical sewage irrigation regions in northern China were observed under the same natural condition by using the soil displacement method at the Luancheng Agro-Ecosystem Experimental Station, Chinese Academy of Sciences. The Station is located in the suburbs of Shijiazhuang City, Hebei Province, covering an area of 0.4 km². It has been designed CNERN (National Ecosystem Research Network of China) land category III B 2 (Warm temperate sub-humid areas) since 1981 and is managed for agro-ecosystem observation and research. It is characterized by intensive and high yield type, resource constraint type and suburban type. The yield two crops a year with maize (Zea mays L.)-wheat (Triticum aestivum L.) represents the cultivation rotation mode of typical farmland in northern China (Fang et al. 2017).

The 0 ~ 20 cm soil layer, which has the relatively concentrated Hg distribution among the whole soil layers (Skylberg et al. 2006) and is closely related with soil-air TGM exchange flux (Ci et al. 2018; Zhou et al. 2017b), was selected as the sampling layer. This soil layer is also in the affected depth of rotary cultivation. Moreover, a special dense plow pan has formed below 20 cm of the farmland by the compaction of agricultural machines. Since this dense plow pan hinders exchanges of soil solution and gas between the upper and lower layers (Fan et al. 2016), deeper soil layer influences the soil-air TGM exchange slightly.

Based on the results of our earlier investigation of soil Hg and other studies in historical sewage irrigation regions (Chen et al. 2012; Cui et al. 2010; Tao et al. 2008; Wang and Zhang 2005), four typical soils once irrigated with sewage in Taiyuan, Tianjin, Shijiazhuang and Xi’an were selected, where the cultivation mode was mainly maize-wheat rotation pattern.

A composite soil sample, composed of five subsamples, was collected using diagonal sampling method at each sampling site. The five subsamples were collected by per 5 cm soil layer and then mixed. Soil samples of 0 ~ 5, 5 ~ 10, 10 ~ 15 and 15 ~ 20 cm were packed in PET bags,
respectively. These 0 – 20 cm soils samples were replaced into the four experimental plots at Luancheng Station and filled into the experimental plots in accordance with the original soil layer order during replacement. The soils below 20 cm in these test plots were undisturbed local soils. Since the farmland soil is disturbed by frequent agricultural activities, soil samples did not experience long-term natural settlement before the observation. This conformed to characteristics of farmland soils. A local farmland experimental plot was built at the same time. All the experimental plots were 1 × 1 m², surrounded by 0.5 m of isolation. The test plots were set up in the middle of the field to avoid the edge effect in crop population. The soils for displacement measurement were meadow cinnamon soil and basic information is showed in Table 1. The planting and management mode of all plots were completely consistent with that of Luancheng Station to keep the same natural conditions in every growth period, and more details are showed in supplementary information S 2.1. The farmlands in northern China are now mostly natural rainfed farmlands. Therefore, all test plots were not irrigated during the observation period. The natural re-emission process of TGM in farmland soils with sewage irrigation history was observed.

**Measurement of soil-air TGM exchange flux**

The soil-air TGM exchange flux was determined by using a coupling method of dynamic flux chamber (DFC) and gold cartridge. The reasons for adopting this method are described in supplementary information S 2.2. This method is widely used to investigate TGM exchange between the surface and air (Eckley et al. 2010; Lin et al. 2012; Zhou et al. 2013). The gold cartridges were sampled from 6:00 to 18:00 and 18:00 to next 6:00, representing daytime (F_d) and nighttime (F_n), respectively (Zhou et al. 2017a), which sampling frequency can effectively reveal the variation of soil-air TGM exchange flux under the canopy of farmland crops. Soil-air TGM flux was calculated by using Equation (1),

$$F_{Don} = Q \cdot \frac{(C_O - C_i)}{A}$$

where $F_D$ or $N$ is the TGM exchange flux (ng m⁻² h⁻¹); $Q$ is the flushing flow through the chamber (0.6 m³ h⁻¹); $A$ is the floor space of the chamber (0.06 m²), $C_O$ and $C_i$ are air TGM concentrations at outlet and inlet of the chamber (ng m⁻³), respectively. The sample flow rate through the gold cartridges was 0.036 m³ h⁻¹. Positive values indicate TGM emission from the surface into the air; negative values indicate TGM deposition to the surface from the air.

According to the TGM exchange data, the single-day cumulative TGM flux ($F$, ng m⁻² d⁻¹) was calculated by using Equation (2)

$$F = (F_d + F_n) \times 12$$

The design of DFC used in this experiment has been adopted by many researchers (Fu, Feng, and Wang 2008; Zhou et al. 2017b). Moreover, the DFCs had been improved in this experiment. More details were showed in S 2.2. Five DFC systems were used to continuously and simultaneously observe soil-air TGM exchange fluxes in different plots, respectively. In addition, another DFC system was used for parallel observation throughout the whole study period.

**Determination of environmental factors**

There is a standard automatic weather station nearby the plots. Furthermore, under the canopy of the test plots, two solar radiation probes (PAR, umol m⁻² s⁻¹), Top Instrument® Model GLZ-C) had been placed at a height of 4 cm above the ground. Three sets of soil temperature and soil moisture probes (Top Instrument® Model TZS-2X) had been plugged into the soils to measure 0 ~ 5 cm soil temperature (°C) and soil moisture (soil volumetric moisture content, %).

The ambient-air TGM was continuous monitoring in the test plots. The five equal length air channels made of Teflon, which were connected to a quartz connector, were set to each plot at 4 cm above the soil. The sample air was mixed in the quartz connector and then entered into the gold cartridge. The sampling frequency and test method were as same as soil-air TGM exchange flux observation.

| Table 1. Basic information of soils for this displacement measurement. |
|---------------------------------------------------------------|
| **Test plot** (Province, basin) | **Location** | **Background of THg (ng g⁻¹)** | **THg (ng g⁻¹)** | **TOM (%)** | **pH** | **Water resources for irrigation** | **History of sewage irrigation** |
| Taiyuan (Shanxi, Fen river) | E 112.4867°, N 37.6925° | 23 | 61.37 ± 0.51 | 6.68 ± 0.45 | 7.93 ± 0.06 | Agricultural sewage | 10 ~ 30 |
| Luancheng (This locality) | E 114.6833°, N 37.8387° | 36 | 81.64 ± 0.44 | 6.58 ± 0.38 | 7.86 ± 0.04 | Groundwater | – |
| Tianjin (Tianjin, North canal) | E 117.0111°, N 39.4797° | 44 | 104.64 ± 0.75 | 6.39 ± 0.32 | 7.80 ± 0.10 | Industrial and sanitary sewage | 30 |
| Shijiazhuang (Hebei, Xiao river) | E 114.7761°, N 37.7177° | 36 | 1042.73 ± 11.39 | 6.84 ± 0.89 | 7.56 ± 0.07 | Industrial and sanitary sewage | 20 ~ 40 |
| Xi’an (Shaanxi, Wei river) | E 108.8881°, N 34.3375° | 60 | 1543.89 ± 35.14 | 6.54 ± 0.15 | 7.58 ± 0.05 | Industrial sewage | 20 ~ 50 |

TOM represents for total organic matter content in soil. The background values of THg were obtained from references (China National Environmental Monitoring Centre, 1994).
Results and discussion

Concentration levels of soil mercury and ambient-air TGM

The soil THg concentration of the test plots was 2.26 – 28.87 times of their local background values (Table 1). The lowest THg in Taiyuan among five plots was about 1.4 times of that in the plow layer of clean irrigation farmland in North China (Song et al. 2015). This indicated that the displacement soils represented sewage-irrigated farmland soils with different Hg contamination levels. The THg at Luancheng plot researched 2.27 times of the local background value, indicating that the farmland in groundwater irrigation region was also at risk of Hg pollution due to the use of chemical fertilizers-pesticides and atmospheric Hg deposition (Hui 2017; Zhang et al. 2019).

The mean ambient-air TGM concentration during the whole study period was 5.06 ± 3.72 ng m⁻³ with a range of 0.89 – 20.13 ng m⁻³. The ambient-air TGM concentration of this rural site in Hebei was 1.57 times than that of Beijing Miyun rural site and higher than most remote sites (Zhang et al. 2013). A study in Shijiazhuang has indicated that the air pollution there is much higher than the majority of megacities around the world (Xie et al. 2019). Earlier studies have indicated that large industrial bases and energy combustions of Hebei are the important regional atmospheric Hg sources (Fu et al. 2015; Zhang et al. 2013). The ambient-air TGM values during the maize (5.45 ± 1.96 ng m⁻³) and wheat growth (3.11 ± 1.91 ng m⁻³) (except two harvests stages) were comparable to the urban sites contaminated by Hg, such as Beijing, Shanghai, Nanjing and Dezhou, China (Duan et al. 2017; Hall et al. 2014; Sommar et al. 2016; Wang et al. 2009; Xie et al. 2019; Zhang et al. 2012; Zhu et al. 2012). In addition, ambient-air TGM concentrations showed obvious seasonal variations in this study. The highest seasonal value was found in two harvests stages with the mean of 11.79 ± 5.04 ng m⁻³ in tillage (maize)-sowing (wheat) and 9.51 ± 6.31 ng m⁻³ in tillage (wheat)-sowing (maize), followed by winter (9.09 ± 4.53 ng m⁻³) and autumn (5.41 ± 2.77 ng m⁻³), lower values occurred in summer (4.50 ± 2.16 ng m⁻³) and spring (2.83 ± 0.88 ng m⁻³), respectively (see Fig. S1). The ambient-air TGM concentration during maize harvest-wheat sowing was higher than the wheat harvest-maize sowing due to the different crop harvest patterns in the two periods. During maize harvest-wheat sowing stage, maize was cultivated by stubble-soil rotary tillage mode, but wheat was harvested by stubble mulch farming mode during wheat harvest-maize sowing. The less disturbance to the stubble-soil, the less increase in ambient-air TGM concentration (Bash and Miller 2007).

The seasonal variations are related to coal combustions, meteorology characteristics, and levels of atmospheric oxidant in Hebei province (Xie et al. 2019; Zhang et al. 2013). As it is reported at the same region in winter, a large number of particulate-bound mercury (PBM), resulting from the consumption of coal for heating, constitutes a substantial fraction of increasing ambient-air TGM during the widespread winter haze (Zhang et al. 2013). Ambient-air TGM concentration in summer was higher to that in spring, which was likely attributed to the strong natural Hg emissions (e.g., soils, vegetations, and water) due to elevated temperature in summer (Liu et al. 2016). Similar ambient-air TGM seasonal variations have been observed in previous studies of forest at northern China (Zhou et al. 2017a).

Temporal variation of soil-air TGM exchange fluxes

As shown in Figure 1(f), the cumulative soil-air TGM exchange fluxes during whole maize-wheat rotation period were as follows: Taiyuan (−23.12 ug m⁻²), Luancheng (23.19 ug m⁻²), Tianjin (25.83 ug m⁻²), Shijiazhuang (244.40 ug m⁻²), Xi’an (507.89 ug m⁻²). The soil-air TGM exchange flux was net deposition during observation period resulted from the lowest of soil THg in Taiyuan plot. This indicated that the concentration gradient of Hg vapor produced in soil was not enough to promote Hg emission under the high ambient-air TGM concentration circumstances. The other plots were showed net Hg emissions. Taking Luancheng as the reference plot, the mean TGM fluxes in Tianjin plots was 1.11 times than that in Luancheng; and the corresponding values in Shijiazhuang and Xi’an were 10.54 and 21.90 times. Note, the soil THg in Tianjin, Shijiazhuang and Xi’an plots were 1.28, 12.77 and 18.91 times than that in Luancheng, respectively. These showed that soil-air TGM exchange fluxes were enhanced one order of magnitude with the increased soil THg from sewage irrigation during the rotation of maize and wheat, indicating sewage irrigation significantly increased TGM evasion from farmland soil. On the other hand, the frequency of Hg deposition (the negative values of soil-air TGM exchange fluxes) in Xi’an plot accounted for 10% of all observation data, which was reduced by half compared with that in Taiyuan plot (Fig. S3 and S4). The results further confirmed that the soil-air TGM exchange fluxes converted from net deposition (Taiyuan) to net emission with the increase of soil Hg pollution caused by sewage irrigation.

As shown in Figure 1 A ~ E, during the whole maize-wheat rotation period, the trends of soil-air TGM exchange fluxes at all plots showed multi-peaks. The emission peaks occurred in the warm seasons of maize and wheat growth, and then declined in the harvests and cold seasons. However, soil-air TGM fluxes were significantly different (one-way ANOVA, p < 0.05) between maize and wheat season. In Figure 1(f), the fluxes all showed net emissions in the maize season, but remarkable depositions in wheat season in Taiyuan, Luancheng and Tianjin plots. For Shijiazhuang and Xi’an plots, the cumulative TGM flux in the maize
The influence of sewage irrigation

The soil-air TGM exchange fluxes during crop growth periods were positive linear correlation with soil THg (Figure 2(a)). The result indicated that THg concentrations may be the dominant factor for controlling the magnitude of soil-air TGM fluxes. Our result was consistent with existing researches from Gustin (2003) and Lin et al. (2010), revealing that TGM flux from soil to atmosphere is significantly dependent on its concentration in soil (O’Connor et al. 2019). Sewage irrigation mainly increases the degree of Hg enrichment in surface soils. (Skyllberg et al. 2006). Then, the formation potential of Hg vapor in the surface layer of the contaminated soil is much greater than that in the background area resulted from the high THg content in the soil at the

season was 5.38 and 3.91 times of that in the wheat season, respectively; and the TGM emissions in maize season accounted for an average of 81.98% of the total TGM emissions during the whole observation period. In Fig. S 2, Fig. S 3 and Fig. S 4, the daytime soil-air TGM exchange fluxes of most plots reached the maximum values at maize jointing-heading stage (August), so did the nighttime fluxes. Although the variation of soil-air TGM fluxes during the wheat season was complicated, we still found that daytime soil-air TGM fluxes were highest in wheat regreening stage with the highest solar radiation reaching the surface soil (March) at most plots and the highest values at nighttime in May with highest soil temperature. Additionally, the promotion of tillage and seeding activities to soil-air TGM emissions only lasted 1 ~ 2 days. In harvest season, the average TGM fluxes increased by 5.13 times in maize and 2.85 times in wheat compared with the average soil-air TGM fluxes during the previous week, respectively. These indicated agricultural activities significantly enhanced the soil Hg evasion from sewage-irrigated farmlands. The commonness and difference of soil-air TGM exchange at these soils coexisted.

Effect of environmental factors on soil-air TGM exchange flux

TGM exchange between different interfaces is determined by TGM concentration gradient and diffusion conditions (Lin et al. 2010). Environmental factors that affect the soil-air TGM exchange mainly include soil pH and TOM (Yang et al. 2007), soil temperature and moisture (Ci et al. 2016), solar radiation (Sizmur et al. 2017) and TGM in ambient-air (Zhou et al. 2016). Since this measurement was not an indoor-control observation, the change of soil-air TGM fluxes with environmental factors was a compound effect of multiple environmental factors. The effect on soil-air TGM exchange flux from THg in soil, soil temperature and soil moisture, solar radiation was based on the data of maize and wheat growing seasons. The data in harvest and tillage periods were excluded because ambient-air TGM concentrations in these two periods were strongly affected by the artificial soil disturbance intensity and duration, which were irregular. And data got during the whole obversion period were used to explore the effect of ambient-air TGM on the soil-air TGM exchange flux. It could avoid the confusion of the effects of human activities on soil-air TGM fluxes when analyzing the effects of natural environmental factors. The detailed discussions are shown below. These results should provide data reference and foundation for future model development.
contaminated sites with a history of sewage irrigation (Gustin 2003). Therefore, these sites were usually the significant source for atmospheric Hg. Compared with soil-air TGM emission from forest (Zhou 2016) and urban (Liu et al. 2014) soil (Figure 2(a)), the slope of fitted curve from farmland was obviously largest, which implied a greater potential from farmland soils than from forest and urban soils. In the early Hg emissions estimation, farmland soil TGM flux was accounted for only about 2% of natural sources (Palinka et al. 2010). Considering the impact of sewage irrigated events, it was likely to underestimate the contribution of Hg emissions from farmland in the existing emissions inventory.

Soil temperature

Figure 2(b) shows the soil-air TGM flux increased with the increasing of soil temperature. When the soil temperature was at around 0°C, all plots showed net TGM deposition. A study has suggested that the TGM in soil air is mainly produced at about 2 cm depth in soil profile (Sigler and Lee 2006). Another study in laboratory shows that the Hg flux is suppressed in general at sub-zero temperatures, too (Corbett-Hains, Walters, and Van Heyst 2012). Therefore, the frozen surface may inhibit TGM emissions from soils. In addition, there was high ambient-air TGM concentration (mean ± SD: 9.09 ± 4.53 ng m⁻³) in winter, which increased the transfer of ambient-air TGM to soil, and this will be discussed in 3.3.5. Furthermore, TGM exchange fluxes changed smoothly at 1 ~ 19°C, and increased rapidly above 19 °C, especially in plots with high soil THg. We checked that 1 ~ 19°C appeared in the wheat season from regreening to heading stages and soil-air TGM fluxes changed smoothly during this period with only a small emission peak at 7 ~ 9 °C during the wheat regreening stage (see Fig. S 2, S 3 and S 4). The early researches in laboratory find that soil TGM flux spikes are evident during positive temperature change or warming (Corbett-Hains, Walters, and Van Heyst 2012; Walters, Glassford, and Van Heyst 2016), and this enhanced TGM flux is the physical evacuation of interstitial pore space gaseous Hg by the expansion and contraction of the freeze-thaw cycle (Corbett-Hains, Walters, and Van Heyst 2012). Early study has indicated that about 80% of the deposited Hg is reemitted back to the atmosphere and 20% of the deposited Hg is retained on the frozen surface (Ferrari et al. 2008), then, TGM emission increases at the onset of frozen surface melt (Durnford et al. 2012). Thin ice layers on the soil surface hindered the absorption and fixation of wet and dry Hg deposited from the atmosphere by functional groups in soil from late October to next February, and then the free Hg could be rapidly reduced.
by photoreduction and re-emitted into the atmosphere once the soil surface thawed during regreening stage of wheat.

Besides, the thick canopy blocked 96% of solar radiation after jointing stage, which resulted in lower variations of soil-air TGM fluxes than that in regreening stage. The sources of TGM in the soil air mainly include the photoreduction of Hg\(^{2+}\) in the soil, microbial reduction and direct reduction of organic matter (Ci et al. 2018; Wang et al. 2009; Zhu et al. 2013). According to the Arrhenius equation, the microbial reduction and direct reduction of organic matter rates should increase exponentially with increasing temperature (Ci et al. 2016; Schlüter 2000). Note, in our study, TGM emission fluxes were decreased a little when the temperature reached 27°C and more. We checked that the higher soil temperature (>27°C) mostly appeared from late July to August, in which the plant height of maize reached the maximum and the canopy had the strongest effect on the shading of light. Although the mean values of soil TGM emissions were highest in this period, the canopy weakened the photoreduction of Hg\(^{2+}\) and reduced the energy transferred to the soil, inhibiting the further increase of TGM emissions from the soil. Additionally, comparing with results from forests soils by Wang et al. (2006), Zhang et al. (2001) and Zhou et al. (2015) (Figure 2(b)), soil temperature could play more important role to enhance soil Hg evasion from the soil in sewage irrigation farmlands.

**Soil moisture**

Precipitation is the main way to increase soil moisture in drylands in northern China. Soil moisture affects soil-air TGM exchange flux by changing the ratio of water to air in soil pore and the distribution of Hg in soil (Briggs et al. 2014; Ci et al. 2016; Gustin and Stamenkovic 2005; Lindberg et al. 1999). As showed in Fig. S 2, when the surface at extremely water-deficient condition (0 – 4 % soil moisture), the soil-air TGM fluxes were extremely low. 0 – 4 % soil moisture values mainly appeared in the days of no precipitation in April and May. Continuous drought and strong attenuation of solar radiation by vegetation inhibited the soil TGM emissions in this period. As soil moisture increasing, more H\(_2\)O molecules will crowd out the Hg molecules originally adsorbed on the surface of the minerals due to the stronger affinity for H\(_2\)O than Hg on soil mineral surfaces (Gustin and Stamenkovic 2005), resulting in a rise of soil TGM evasion fluxes. In the study region, it rained in hot season during maize season which was beneficial to the evaporation of water and accelerate the Hg transfer rate to the interface in maize season. However, some studies have shown that under high soil moisture conditions (close to soil moisture saturation), and excessive water will cause a significant decrease in soil TGM fluxes (Ci et al. 2016; Zhou et al. 2017b). In this study, soil moisture values were 18.80 ± 6.43 % in maize season and 8.09 ± 7.32 % in wheat season, respectively. Obviously, the both soil moisture values were less than the soil moisture saturation (about 40%), so the inhibitory effect of soil moisture on soil-air TGM emission was not observed (see Figure 2(c)). Previous study on soil-air TGM fluxes in forest in northern China also showed that the soil moisture varies from 2% to 30% and the increase of soil moisture is beneficial to the generation of TGM in soil air in this range (Zhou 2016).

**Solar radiation**

Many studies have summarized that the increasing intensity of solar radiation will stimulate more Hg\(^{2+}\) photoreduction (especially UV), then raise the concentration of TGM in the soil air, resulting in promoting TGM emissions sharply (Bonzongo and Donkor 2003; Moore and Carpi 2005) and the change of solar radiation will also lead to the changes in soil temperature which will affect the rate of soil-air TGM exchange flux at night (Bonzongo and Donkor 2003; Moore and Carpi 2005). In this study, the ratios of soil-air TGM flux in daytime to that in nighttime were showed in Figure 2(d). It was clear that the ratios were stabilized with 3.94 ± 0.10 in the maize season among five plots with different soil THg levels. For the wheat season, the ratios fluctuated slightly but no significant difference (3.41 ± 0.65, P < 0.05, one-way ANOVA) was found among the five plots. As shown in Fig. S 2, the ratios of soil temperature, soil moisture and ambient-air TGM in daytime and nighttime were relatively stable in the maize season and the ratios were 1.02 ± 0.06, 1.01 ± 0.06 and 0.85 ± 0.32, respectively. Moreover, the ratios were 1.15 ± 0.67, 1.24 ± 0.50 and 0.99 ± 0.77 in wheat season, respectively. These results suggested that the most obvious difference between daytime and nighttime was the solar radiation throughout the day. It may indicate that the promotion effect of solar radiation on the soil-air TGM exchange should be approximately 3.41 ~ 3.94 times. This will be beneficial for estimating the soil-air TGM fluxes.

**Total gaseous mercury in ambient air**

A bimodal pattern of soil-air TGM exchange flux was shown with the increased of ambient-air TGM (see Figure 3(a)). As mentioned in 3.2, when we plowed and sown the test plots, the soil-air TGM exchange fluxes of these plots did rapidly increase due to soil disturbance. In harvests, the emission plumes from the other tilled areas of the field meandered, dispersed slowly and rise over the adjacent area, which caused the soils of our plots to become seasonal reservoirs of atmospheric Hg (see Fig. S 2, S 3 and S 4). However, Hg emission peak swiftly appeared
when the ambient-air TGM gradually decreased (October 10 ~ 16). The results suggested that the variation of soil-air TGM fluxes were very sensitive to the variation of ambient-air TGM. Our results were consistent with the earlier observations that Hg from atmospheric deposition and leaf litter fall can evade to the atmosphere by large amounts when the soil is disturbed (Bash and Miller 2007; Biester, Müller, and Schöler 2002; Niu et al. 2011; Sheehan et al. 2006). The cultivation is the main characteristics distinguishing agro-ecosystems from other terrestrial ecosystems. The rapid change of TGM exchange direction between soil and air was also one of the seasonal characteristics of TGM exchange in farmlands.

There were significant negative correlations at all the five test plots between soil-air TGM exchange flux and ambient-air TGM concentration during maize (−0.16* ~ −0.27**, p < 0.05) and wheat (−0.32** ~ −0.89**, p < 0.01) seasons, respectively (see Table S 1). The ambient-air TGM concentration at which no net TGM exchange occurs between the air and soil (mean TGM flux equal to zero) is termed the air compensation point for the soil (Xin and Gustin 2007). Negative correlation linear regression analyses were performed to determine the compensation points of soil-air TGM exchange. Figure 3(b) shows the variation of compensation points of soil-air TGM exchange with soil THg, which revealed an exponential increasing correlation during maize growth and a linear correlation during wheat growth. The compensation points were higher during the growing period of maize than those of wheat in all test plots. Higher soil temperature, soil moisture, and stronger solar radiation kept enhancement TGM emission rate in maize growth. The soil THg in Xi’an plot was 25.16 times higher than that in Taiyuan, but the compensation point of soil-air TGM exchange in Xi’an was only 2.39 (in maize) to 4.55 (in wheat) times higher than that in Taiyuan. And the growth rate of the compensation points gradually slowed down with the increase of soil THg concentration in summer maize season. It suggested that the rate of TGM formation in soil–air interface might become the main limiting potential of TGM emission from soils, and the increase of soil THg could not increase the soil TGM emission potential indefinitely. The increase of ambient-air TGM played a key role in inhibiting the process of soil TGM release.

Conclusions

Soil-air TGM exchange fluxes from farmlands with sewage irrigation history deserve attention. In this paper, the soil-air TGM exchange fluxes of historical sewage irrigated farmlands with different Hg polluted levels in northern China were observed by soil replacement method under the same environment and planting conditions. The soil-air TGM exchange fluxes converted from net deposition (Taiyuan) to net emission with the increase of soil Hg pollution caused by historical sewage irrigation. The results of the present study showed that historical sewage irrigation significantly increased TGM evasion from soil. The response rules of soil-air TGM fluxes to environmental factors at sewage and clear irrigated farmlands were basically consistent. Generally, it was the source of atmospheric TGM from spring to autumn but the sink in winter and seasonal harvests. The ratios of soil-air TGM flux in daytime to that in nighttime were 3.94 during maize growth and 3.41 during wheat growth, which showed little affected by soil Hg concentration. This seemed to reveal the ability of solar radiation to promote TGM emission under natural condition. The response of TGM exchange to soil temperature rise under natural conditions was not a simple positive correlation. There was a small soil TGM emission peak in the temperature range of 7 ~ 9 °C, then the emission rate rose rapidly in the temperature range of 19 ~ 27 °C, which was the dominant temperature of TGM emission in natural farmlands. The soil TGM emission was inhibited a further
increase due to the dense crop canopy, when soil temperature was higher than 27 °C. While, the increase of soil moisture in the range of 0 ~ 30% mainly promoted the soil TGM emission, which might be related to the unsaturated state of soil moisture in the northern China under the natural precipitation. The compensation point of soil-air TGM exchange was increased with enhancement soil Hg level, and yet ambient-air TGM played a key role for soil Hg evasion. Comparing with forest and urban soil, the evasion of TGM from sewage irrigated farmlands with high Hg concentrations may be potential hotspots of Hg in the atmosphere, and it was likely to underestimate Hg emissions from farmlands in the existing emissions inventory. Additional regional investigations and process-level researches are needed to better understand the role of farmlands with sewage irrigation history in local and global biogeochemical cycles of Hg.

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Disclosure statement

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