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Real-time on-site monitoring of soil ammonia emissions using membrane permeation-based sensing probe^{\star}

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ABSTRACT

An ability to real-time, continuously monitor soil ammonia emission profiles under diverse meteorological conditions with high temporal resolution in a simple and maintenance-free fashion can provide the urgently needed scientific insights to mitigate ammonia emission to the atmosphere and improve agricultural fertilization practice. Here, we report an open-chamber deployment unit embedded a gas-permeable membrane-based conductometric sensing probe (OC-GPMCP) capable of on-site continuously monitoring soil ammonia emission flux (J_{NH_3}) –time (t) profiles without the need for ongoing calibration. The developed OC-GPMCPs were deployed to a sugarcane field and a cattle farm under different fertilization/meteorological conditions to exemplify their real-world applicability for monitoring soil ammonia emission from agricultural land and livestock farm, respectively. The obtained J_{NH_3} – t profiles from the sugarcane field unveil that the ammonia emission rate is largely determined by fertilization methods and meteorological conditions. While the J_{NH_3} – t profiles from the cattle farm can be decisively correlated to various meteorological conditions. The reported OC-GPMCP is cheap to fabricate, easy to deploy, and maintenance-free to operate. These advantageous features make OC-GPMCP an effective analytical tool for large-scale soil ammonia emission assessment under diverse meteorological conditions, providing critically important scientific insights to mitigate ammonia emission into the atmosphere and improve agricultural fertilization practice.

1. Introduction

Nitrogen fertilizers are widely used in modern agricultural practice to enhance crop's productivity. Although \sim 1.2 % of global energy has been consumed to produce nitrogen fertilizers, over 60 % of the applied nitrogen fertilizer is lost to the aquatic environment and atmosphere through water runoff and volatilization before being utilized by crops (Canfield et al., 2010; Wang et al., 2018). Other than the agricultural sector, ammonia also emits from other sources such as livestock farms (Ti et al., 2019), landfill sites (He et al., 2011), wetlands (Luo et al., 2016), and mangroves (Biswas et al., 2005), accounting for \sim 20 % of global ammonia emissions (Agency, 2015; Meng et al., 2017; Paulot et al., 2014). To date, Although both the eutrophic impact of agricultural nitrogen fertilizer runoff on aquatic systems and the environmental impact of agricultural ammonia emissions on the atmosphere have been extensively reported (Abell et al., 2019; Cheng et al., 2016; Jain et al., 2020; Smith et al., 1999; Wu et al., 2016; Zak et al., 2018), the sensing techniques employed for monitoring agricultural ammonia emissions are complex and labour intensive. Therefore, developing simple and effective analytical techniques capable of real-time, continuously monitor soil ammonia emission profiles under diverse meteorological conditions with high temporal resolution in a simple and maintenance-free fashion can provide the needed scientific insights to mitigate ammonia emissions to the atmosphere and improve

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Currently, the micro-meteorological and chamber-based methods are commonly used to measure soil ammonia emission/volatilization. The micro-meteorological methods determine the soil ammonia emission flux (J_{NH_3}) based on various quantification principles such as mass balance (Häni et al., 2016; Yang et al., 2019), gradient diffusion (Hayashi et al., 2011; Sommer et al., 2004), vorticity correlation (Nelson et al., 2017a; Sun et al., 2015) and equilibrium concentration (Mattila and Joki-Tokola, 2003; Saarijärvi et al., 2006). With an integrated ammonia detector (e.g., differential optical absorption spectroscopy (Mount et al., 2002)), the micro-meteorological methods are capable of directly detecting soil J_{NH_3} in a non-invasive manner under the natural environment (Bell et al., 2017; He et al., 2014; Schilt et al., 2004; Warland et al., 2001). However, the setup and successive operation of such methods involve high capital costs and tedious procedures, and require considerable technological input and highly-trained personnel (Insausti et al., 2020). The existing chamber-based methods include wind tunnel, closed-chamber, and ventilated-chamber methods. The wind tunnel method utilizes an air pump to flow air through a tunnel chamber, where ammonia volatilization for a given period is determined according to the "wind" speed and ammonia concentration difference between the entry and exit points of the tunnel (Watt et al., 2016). The method, on the one hand, enables easier control of micrometeorological conditions, while on the other hand, the overlying tunnel chamber hinders the accurate control of the static wind conditions, leading to inaccurate results (Calvet et al., 2013; Hudson et al., 2009; Parker et al., 2013). The relatively high setup costs and the needed ammonia detection for a large number of samples in the laboratory are also major drawbacks of the method. Till now, due to their advantages of simple and portable configurations, cheap to fabricate, and easy to deploy and operate, the closed-chamber and ventilated-chamber methods are the most frequently used methods to measure soil ammonia volatilization (Amin, 2020; Parker et al., 2013; Yao et al., 2020). Both methods employ a reservoir of a weak acid (e.g., phosphoric acid/boric acid in solution or adsorbed on sponges) as the absorbent to collect the volatilized ammonia from soil for a given period under natural or ventilated conditions. The ammonia contents in the resultant absorbents are analyzed by back-titration in laboratory and used to calculate soil $J_{\it NH_3}.$ As such, these methods are essentially the sample collection methods with serious drawbacks including laborious procedures, low sensitivity and poor temporal resolution.

The development of easily implementable gas sensors capable of onsite monitoring ammonia emissions in a rapid, sensitive, accurate and continuous manner is obviously required as it can offer the urgently needed analytical tool to enable systematically studying soil ammonia emission behaviors and acquiring critical scientific insights to improve ammonia emissions control and management practices (Insausti et al., 2020). In this regard, we have developed a portable probe (Li et al., 2017) and successfully applied it to on-site, real-time, continuously monitor ammonia emission from a rice field with a closed-chamber configuration (Li et al., 2019). In this work, we report an open-chamber deployment unit embedded a gas-permeable membrane-based conductometric sensing probe (OC-GPMCP), enabling ammonia emission monitoring under diverse meteorological conditions. Importantly, a refined analytical principle for the open-chamber deployment unit is developed to empower OC-GPMCP for directly acquiring soil ammonia emission flux in a real-time and continuous manner with high temporal resolution. The developed OC-GPMCPs were applied to on-site monitor J_{NH_3} from sugarcane field and cattle farm under different fertilization/meteorological conditions in a simple and maintenance-free fashion to exemplify their real-world applicability. The obtained $J_{NH_3} - t$ profiles from the sugarcane field unveil that the ammonia emission rate is largely dictated by the fertilization methods and meteorological conditions, while the $J_{NH_3} - t$ profiles from the cattle farm can be decisively correlated to various meteorological conditions. Deferring markedly from all existing soil ammonia monitoring systems,

the reported OC-GPMCP is a simple device that is cheap to fabricate, easy to deploy and maintenance-free to operate, ranking it an ideal monitoring tool for large-scale soil ammonia emissions assessment under diverse meteorological conditions.

2. Materials and methods

2.1. Chemicals and materials

All chemicals used in this study were of analytical grade or equivalent. All solutions were prepared using deionized water (Millipore Corp., 18.2 M Ω cm). The boric acid solution (0.5 M) was prepared and used as the receiving solution in the sensing probe. An aqueous solution containing 0.8 M phosphoric acid and 0.7 M glycerol was used to induce adsorbent onto sponges for measuring ammonia volatilization flux by a conventional method (Nômmik, 1973). A DuraporeTM PVDF membrane (diameter: 47 mm, thickness: 125 μ m, average pore size: 0.1 μ m, porosity: 70 %) was used as the gas-permeable membrane.

2.2. Sensing system setup

The GPMCP reported in our previous work (Li et al., 2017) was employed as the ammonia sensing probe. As shown in Fig. S1, an OC-GPMCP consists of a GPMCP (loaded with 2.00 mL boric acid receiving solution), a temperature sensor, and a cylindrical-shaped sensing chamber (height: 12 cm; internal diameter: 6 cm) with two legs (3 cm) to anchor the unit on soil. A GPMCP was installed inside the sensing chamber 2 cm above the soil/sample solution surface. Fig. S2 schematically illustrates the monitoring system setup. Briefly, up to 8 sensing units can be directly connected to a home-made data logger/controller equipped with a modem to wirelessly communicate with the computer connected to a wireless receiver for real-time operational control and transfer/processing analytical data.

2.3. Laboratory experiment

Fig. S3 shows the experimental setup for laboratory validation experiments. A 12.5 L (0.25 \times 0.25 \times 0.2 m³) open sample container containing 4.0 L solutions with different NH₄Cl concentrations was used to controllably generate the desired ammonia volatilization fluxes by adding sufficient amounts of 5 M NaOH to bring the source solution pH > 12. For a typical experiment, one OC-GPMCP, five conventional chamber measurement units together with a temperature sensor and a pH sensor were placed in the sample container. The sample container was placed in a thermotank to ensure a constant temperature. Unless otherwise stated, all validation experiments were conducted at 25 °C. The OC-GPMCP continuously acquired the conductivity changes at a frequency of 10 s per data point and used to determine ammonia volatilization fluxes at a frequency of 5 min. For confirmation purpose, the gaseous ammonia fluxes were also measured by a chamber-based method developed by Nömmik (Nômmik, 1973). The sampling devices used for the chamber-based method were made of a cylindrical chamber (height: 11 cm, internal diameter: 6 cm) and each embedded two sponge discs (diameter: 7 cm, thickness: 2 cm) impregnated with phosphoric acid/glycerol adsorbent to trap the volatilized ammonia. One sponge disc was placed at the open end of the cylindrical chamber to prevent interference from external ammonia, while the second sponge disc was installed 2 cm below the first disc to capture the ammonia volatilized from the targeted sample surface. The trapped ammonia in the second sponge disc was extracted according to the reported method (Nômmik, 1973) and analyzed by the standard indophenol blue method to calculate the corresponding ammonia volatilization flux every 5 min (Baird, 2017).

2.4. Field deployment

Two deployment sites, a sugarcane field and a cattle farm, in Southeast Queensland (Fig. S4a), were selected to demonstrate the applicability of OC-GPMCP to real-time monitoring soil ammonia volatilization for agriculture and livestock scenarios. The selected sugarcane field was covered predominantly by the sandy loam topsoil interspersed with fine roots and sugarcane debris (Fig. S4b). For a typical field measurement cycle, three OC-GPMCPs were deployed to the selected site and located ${\sim}50~\text{cm}$ apart from one and another. The temperature sensors were also deployed to simultaneously record temperature profiles. In order to simulate the fertilization-induced change in ammonia volatilization fluxes, urea was used as the nitrogen fertilizer. The same amount of urea (100 mg, equivalent to 165 kg N ha^{-1}) was respectively applied to the soil surface and 4 cm under the soil surface where the OC-GPMCP#1 and #2 were deployed. No fertilizer was applied to the deployment site of OC-GPMCP#3. The selected cattle farm was over 50 acres and held 80 cattle that were grazed in the pasture and also fed with grains in a stockyard. Three OC-GPMCPs were deployed at a selected location to monitor the ammonia volatilization fluxes from the stockyard surrounding environment (Fig. S4c).

3. Results and discussion

3.1. Quantitative $R_{CI} - J_{NH_3}$ relationship

As illustrated in Fig. 1a, the OC-GPMCP used in this work is constructed by assembling a GPMCP into a cylindrical-shaped sensing chamber. The cylindrical chamber is used to confine a measurement environment where the disturbance on the natural volatilization process by tangential airflow is prevented. The purposely designed gap between GPMCP and chamber wall, and the opened chamber structure enable free movements of the volatilized ammonia ($\{NH_3\}_g$) to avoid any accumulation effect. In this work, boric acid (H_3BO_3) is used as the receiving solution. As illustrated in Fig. 1b, once such an OC-GPMCP is deployed, the emitted $\{NH_3\}_g$ from soil through volatilization process instantaneously transports across the gas-permeable membrane (GPM) and stoichiometrically reacts with H_3BO_3 at the inner membrane interface to form electrically conductive NH_4^+ cation and $B(OH)_4^-$ anion (Eq. (1)):

$${NH_3}_{aq} + H_3BO_3 + H_2O \rightarrow NH_4^+ + B(OH)_4^-$$
 (1)

Due to the free movement of the volatilized ammonia, the $\{NH_3\}_g$ partial pressure exerted on the outer interface of GPM ($P_{NH_3}^{Outer}$) should be directly proportional to the soil ammonia volatilization flux (J_{NH_3}):

$$P_{NH_3}^{Outer} \propto J_{NH_3} \tag{2}$$

It is well known that the instantaneous flux of $\{NH_3\}_g$ transport across GPM $(J_{NH_2}^{GPM})$ is directly proportional to the ammonia partial

pressure difference between the outer and inner interfaces of GPM $(dP_{NH_3} = P_{NH_3}^{Outer} - P_{NH_3}^{Inner})$. Due to the rapidity of acid-base reaction, the transported $\{NH_3\}_g$ will be immediately consumed by H₃BO₃, leading to an essentially zero $\{NH_3\}_g$ partial pressure at the inner GPM interface $(P_{NH_2}^{Inner} = 0)$. That is:

$$dP_{NH_3} = P_{NH_3}^{Outer} \propto J_{NH_3}^{GPM} \tag{3}$$

According to Eq. (1), the rate of conductivity increment $(R_{CI} = \frac{dx}{dt})$ in the receiving solution should be directly proportional to the per unit time increased NH₄⁺ number $(\frac{dN_{NH_4^+}}{dt})$ in the receiving solution. Considering the stoichiometric reaction of $\{NH_3\}_g$ with H₃BO₃, $\frac{dN_{NH_4^+}}{dt}$ must be proportional to dP_{NH_3} . According to Eqs. (2) and (3), we have:

$$R_{CI} = \frac{d\sigma}{dt} \propto \frac{dN_{NH_4^+}}{dt} \propto J_{NH_3}^{GPM} = K \bullet J_{NH_3}$$
(4)

where, $N_{NH_4^+}$ is the number of NH₄⁺ in the receiving solution and *K* is the probe constant of OC-GPMCP, depending on the GPM's properties and exposed area, characteristics of the embedded conductivity detector, receiving solution volume and operational temperature. This means that the soil ammonia volatilization flux can be directly determined from the measured R_{CI} once *K* is known. In practice, for a given temperature, each OC-GPMCP has its own *K* value that can be experimentally determined. Importantly, once *K* for an OC-GPMCP is determined and corrected for temperature effect, no ongoing calibration is needed during deployment. Such an advantageous feature makes OC-GPMCP a very attractive field-based analytical tool to on-site monitor soil ammonia volatilization (Insausti et al., 2020).

3.2. Validation of $R_{CI} - J_{NH_3}$ relationship

In order to validate the $R_{CI} - J_{NH_3}$ relationship defined by Eq. (4), an unsealed sample container filled with 4.0 L solutions containing different concentrations of NH₄Cl (Fig. S3) were used to controllably generate different ammonia volatilization fluxes by adding sufficient amounts of NaOH to bring the source solution pH > 12 at 25 °C. The volatilization fluxes generated from different concentrations of NH₄Cl were determined by a well-known conventional chamber-based method developed by Nömmik (Nômmik, 1973). For each NH₄Cl solution, one OC-GPMCP and five conventional chamber measurement units were deployed 5 min after the NaOH was added. During the measurement, one conventional chamber measurement unit was withdrawn every 5 min and the volatilized ammonia adsorbed by the sponge disc was analyzed by the standard indophenol blue method to calculate the corresponding average ammonia volatilization flux over 5 min period (Baird, 2017). As shown in Fig. S5a, b, for all cases investigated, the steady J_{NH3} can be attained 10 min after adding NaOH. A plot of NH₄Cl concentration in the solution against the steady J_{NH_3} measured by the chamber method gives a near perfect linear relationship (Fig. S5c),



Fig. 1. (a) Schematic diagram of OC-GPMCP sensing unit configuration and deployment; (b) Schematic diagram illustrating ammonia volatilization flux monitoring principle.

confirming that for a given temperature, the J_{NH_3} generated from a given NH₄Cl solution has a fixed value. According to Eq. (4), under a constant temperature, for a given NH_4Cl solution, R_{Cl} is a fixed value. This means that if Eq. (4) is correct, for a given NH₄Cl solution, the receiving solution conductivity (σ_{25}) must increase linearly with the deployment time (*t*) because R_{CI} is defined as the slope of $\sigma_{25} - t$ plot. Fig. 2a and b shows the simultaneously recorded $\sigma_{25} - t$ profiles under the steady-state ammonia volatilization conditions (15 min after adding NaOH) from the same set of NH₄Cl solutions used for Fig. S5. Under such steady-state ammonia volatilization conditions, linear σ_{25} – t relationships are obtained from all cases investigated, signifying the predicted relationship by Eq. (4). Eq. (4) also predicts a directly proportional relationship between R_{CI} and J_{NH_3} . As unveiled by Fig. 2c, a plot of R_{CI} against J_{NH_3} gives a perfect linear line ($R^2 = 0.997$), confirming the validity of Eq. (4). According to Eq. (4), the probe constant, *K* can be derived from the slope of $R_{CI} - J_{NH_3}$. In this case, K (OC-GPMCP#1) = 8.47 μ S cm μ g⁻¹ at 25 °C.

Validation experiments were also carried out to further confirm the reliability of OC-GPMCP determined J_{NH_3} . Fig. S3 shows the validation experimental setup. Different steady-state ammonia emission fluxes were generated by adding an appropriate amount of 5 M NaOH solution to a set of solutions containing different concentrations of NH₄Cl (pH > 12). Under the steady-state ammonia emission conditions. OC-GPMCP#1 with an exposed membrane area of 7.07 cm² that loaded with 2.00 mL of 0.50 M H₃BO₃ receiving solution was deployed in the measurement chamber (Fig. S3) to real-time record $\sigma_{25} - t$ curves over a 5 min period (Fig. S6). The corresponding ammonia emission fluxes $({J_{NH3}})_{OC-GPMCP})$ were quantified by Eq. (4) with the predetermined $K_{\text{OC-GPMCP}\#1} = 8.47 \ \mu\text{S cm} \ \mu\text{g}^{-1}$ (Table S1). After each $\{J_{NH3}\}_{\text{OC-GPMCP}}$ measurement, the ammonium concentration $([NH_4^+])$ in the receiving solution was determined by the standard indophenol blue method (Baird, 2017) and used to calculate $\{J_{NH3}\}_{STD}$ (Table S1) in accordance with Equation (5):

$$\left\{J_{NH_3}\right\}_{STD} = \frac{\left[\mathrm{NH}_4^+\right]\left(\mu\mathrm{g}\ \mathrm{L}^{-1}\right) \times \mathrm{V}\ (\mathrm{L})}{S(cm^2) \times t(\mathrm{min})}$$
(5)

where, $V = 2.00 \times 10^{-3}$ L, S = 7.07 cm², t = 5 min.

The determined $\{J_{NH3}\}_{\text{STD}}$ based on the receiving solution $[\text{NH4}^+]$ quantified by the standard indophenol blue method should be highly reliable. The correlation analysis was then carried out to determine the correlation coefficient between $\{J_{NH3}\}_{\text{OC-GPMCP}}$ and $\{J_{NH3}\}_{\text{STD}}$ (Fig. S7). The unveiled correlation coefficient of 0.997 and the near unity slope value of 0.96 confirm that measured ammonia emission fluxes by both methods are closely approximate to each other.

3.3. Analytical performance

Important analytical performance indicators were evaluated. The sensitivity of OC-GPMCP can be defined by the per unit time conductivity change caused by per unit of ammonia volatilization flux transport across the GPM, which equals the probe constant, *K*. For OC-GPMCP#1 used in this work, K (25 °C) = 8.47 µS cm µg⁻¹. That is, an ammonia

volatilization flux of 1 μ g cm⁻² min⁻¹ will increase the conductivity by 8.47 μS cm⁻¹ over 1 min. As shown in Fig. 2, OC-GPMCP#1 can readily determine the ammonia volatilization fluxes ranged from 0.002 to $0.272 \ \mu g \ cm^{-2} \ min^{-1}$. It should be mentioned that the sensitivity and analytical linear range of OC-GPMCP can be readily altered by changing the dimensional parameters of the embedded GPMCP and deployment time. For example, as K is directly proportional to the exposed GPM area (S) and inversely proportional to the receiving solution volume (V), the sensitivity can therefore be increased by increasing S and decreasing V. In addition, the membrane regulated ammonia transport process makes OC-GPMCP an accumulative method. This means that for a given OC-GPMCP, the sensitivity can be increased by simply increase the deployment time; however, an increased sensitivity by altering dimensional parameters always leads to a decreased analytical linear range. An investigation was therefore carried out to extend the linear range without compromising sensitivity. Considering the analytical linear range is dictated by the linearity of $\sigma_{25} - t$ profile and due to the accu-

mulative nature (
$$\sigma_{25}=\int rac{d\sigma}{dt} dt$$
), the analytical linear range of an OC

GPMCP can be estimated from $\sigma_{25} - t$ plot under a constant J_{NH_3} . As shown in Fig. S8, for a given OC-GPMCP with a fixed receiving solution volume under a constant J_{NH_3} , an increased H₃BO₃ concentration in the receiving solution leads to an increase in the required time to deviate $\sigma_{25} - t$ plot from linear response without noticeably decreased sensitivity (the slope of $\sigma_{25} - t$). Under the measurement conditions, the $\sigma_{25} - t$ plot linear range markedly increased from 460 to 4362 µS cm⁻¹ when the H₃BO₃ concentration is increased from 0.1 to 0.5 M (Table S2). According to previous studies, the agricultural soil ammonia emission flux is usually <0.05 µg cm⁻¹ min⁻¹ (Nelson et al., 2017b; Singh et al., 2013; Yang et al., 2015). Therefore, when the receiving solution concentration of an OC-GPMCP is increased from 0.1 to 0.5 M, the continuous monitoring capacity for an ammonia emission flux of 0.05 µg cm⁻¹ min⁻¹ is increased from ~18 to ~171 h.

3.4. Pre-calibration

Currently, almost all of the reported agricultural soil ammonia emissions monitoring techniques need to perform frequent ongoing calibration, which involves laborious procedures and requires welltrained personnel (Insausti et al., 2020). According to Eq. (4), for a given OC-GPMCP, the probe constant (*K*) depends only on the operational temperature (*T*). This means that once an OC-GPMCP's *K* – *T* relationship is determined before deployment, no ongoing calibration is needed for the subsequent application (Li et al., 2017). The operational temperature affects *K* because it affects the receiving solution conductivity and the rate of ammonia transport across GPM. A two-step precalibration strategy was therefore adapted to determine K - Trelationship. For a given OC-GPMCP, conductivities measured at different temperatures (σ_T) are firstly normalized to σ_{25} (the conductivity value at 25 °C) and then used to establish a probe-specific K - Trelationship.



Fig. 2. (a, b) $\sigma_{25} - t$ profiles obtained by OC-GPMCP#1 under different J_{NH_3} ranging from 0.002 to 0.272 µg cm⁻² min⁻¹ generated from the solutions containing different NH₄Cl concentrations; (c) $R_{CI} - J_{NH_3}$ plot (data are derived from Fig. 2a and b).

Three OC-GPMCPs were employed in this work. The $\sigma_{\rm T} - T$ profiles from OC-GPMCP#1, #2 and #3 with 0.50 M H₃BO₃ as the receiving solution were measured (Fig. S9) and used to derive the corresponding $\sigma_{25} - T$ relationships (Eq. (5)).

$$\sigma_{25}(\text{OC} - \text{GPMCP}\#1) = \sigma_T + 1.163(25 - T)$$
(5a)

$$\sigma_{25}(\text{OC} - \text{GPMCP}\#2) = \sigma_T + 1.090(25 - T)$$
(5b)

$$\sigma_{25}(\text{OC} - \text{GPMCP}\#3) = \sigma_T + 1.216(25 - T)$$
(5c)

The slope of each $\sigma_T - T$ linear equation (the conductivity change per unit temperature) represents the temperature effect on the detected σ value by the conductivity detector embedded in the corresponding OC-GPMCP. Eq. (5) was embedded in the data processing software and used to real-time converted the measured σ_T to σ_{25} according to the measured temperature.

In order to obtain K - T relationship, 7 sets of $\sigma_{25} - t$ curves were obtained from each OC-GPMCP under different temperatures ranged from 10.6 to 40.3 °C (Figs. S10a-g, -12a-g). Each set of $\sigma_{25} - t$ curves from different J_{NH_3} under a given temperature was used to construct an $R_{CI} - J_{NH_3}$ plot to determine the corresponding K of the temperature (Figs. S10a-g, -12a-g). The K - T dependent relationships (Eq. (6)) were determined by plotting K against temperature (Figs. S10h -12h).

$$K(T, OC - \text{GPMCP}\#1) = 0.0065T + 8.305$$
 (6a)

K(T, OC - GPMCP#2) = 0.0073T + 8.597(6b)

$$K(T, OC - \text{GPMCP}\#3) = 0.0057T + 8.192$$
(6c)

The slope of K - T plot defines the temperature effect on the probe constant. Eq. (6) was embedded in the data processing software and used to real-time correct *K* according to the measured temperature.

3.5. Field applications

To demonstrate the real-world applicability, three pre-calibrated OC-GPMCPs (OC-GPMCP#1, #2 and #3) were deployed at the two selected sites, a sugarcane field and a cattle farm in Southeast Queensland (Fig. S4). Two temperature sensors were co-deployed at each site to continuously monitoring air temperature. Meteorological information for the deployment periods was obtained from the Australian Bureau of Meteorology (www.bom.gov.au). The soil pH of each site was determined according to a reported method (Schofield and Taylor, 1955). The σ_{25} data were collected at a frequency of 10 s per data point, while J_{NH_3} was determined every 5 min according to Eq. (4) using K (T) and R_{CI} derived from the recorded $\sigma_{25} - t$ profile over the corresponding period.

The sugarcane field was selected to demonstrate the applicability of OC-GPMCP to monitor soil ammonia emissions for agricultural lands. Over a 72 h deployment period between 10:30 a.m. May 19, 2020–10:30 a.m. May 22, 2020, the commercially supplied urea was applied as the nitrogen fertilizer (165 kg N ha⁻¹) to simulate the fertilization induced change in ammonia volatilization fluxes *via* two typical sugarcane farming fertilization practices (surface and subsurface fertilization approaches) (Calcino et al., 2018). OC-GPMCP#1 and #2 were deployed at the locations with surface and subsurface fertilization (right before the deployment), respectively, while the OC-GPMCP#3 was deployed at the location without the fertilizer application. The soil pH at the site was determined to be ~6.86.

Fig. 3 shows the real-time determined $J_{NH_3} - t$ profiles by the deployed OC-GPMCPs together with the air temperature profile as well as rainfall record over the deployment period. The reported $J_{NH_3} - t$ profiles were derived from the corresponding $\sigma_{25} - t$ profiles shown in Fig. S13. Over the deployment period, the air temperature fluctuated between 14.7 and 24.0 °C, and several rainfall events with 0.2–6 mm precipitations were recorded. It can be seen from Fig. 3, the determined $J_{NH_3} - t$ profile (red) by OC-GPMCP#3 without the applied fertilizer



Fig. 3. $J_{NH3} - t$ profiles obtained by OC-GPMCP#1 from the sugarcane field with different fertilization methods, and the recorded temperature profile and precipitation data during the deployment period. The grey shields indicate night-time. The presented $J_{NH3} - t$ profiles are derived from the corresponding $\sigma_{25} - t$ profiles shown in Fig. S13.

exhibits an almost constant J_{NH_3} (~0.0010 µg cm² min⁻¹) over the entire deployment period, regardless of the changes in meteorological conditions. Such a low level of J_{NH_3} could be due to the relatively low NH_4^+ content in the soil combined with the slightly acidic soil pH (6.86). The determined $J_{NH_3} - t$ profile (black) by OC-GPMCP#2 from the subsurface fertilization site reveals that during the initial 26 h (\sim 10:30 a. m. 19/05-12:30 p.m. 20/05), despite six rainfall events with a total perception of 9.0 mm, the recorded J_{NH_3} is at a similar level as that recorded from the case without applied fertilizer. A gradually increase in J_{NH_3} was observable from ~12:30 p.m. 20/05, followed by a noticeably accelerated increase in J_{NH_3} at ~9:00 a.m. 21/05, dropped slightly between \sim 1:30–6:30 a.m. 22/05, and started to increase again at \sim 8:00 a. m. 22/05. Based on the time-weighted integration of the real-time determined J_{NH_3} , the lost fertilizer through ammonia emission over the 3-day deployment period is found to be 3.59 kg N $\rm ha^{-1}$ (7.70 kg urea ha^{-1}), corresponding to a 4.7 % loss of the applied urea. It seems that the rate of ammonia emission is not noticeably influenced by the change of meteorological conditions during the initial ~48 h. However, the two upsurge ammonia emission periods observed during 21st and 22nd of May could be correlated to the daylight-induced temperature rise. In sharp contrast, when urea was directly applied to the soil surface, the determined $J_{NH_3} - t$ profile (orange) by OC-GPMCP#1 during the initial period unveils obviously higher ammonia emission rates than the case of the sub-surface fertilization. A rapidly and almost linearly increased J_{NH_3} were observed between \sim 5:00–10:00 p.m. 19/05, slowed down at 10:00 p.m. 19/05, accelerated again at 7:00 a.m. 20/05 to reach the peak emission of $J_{NH_3} = 0.075 \,\mu \text{g cm}^2 \,\text{min}^{-1}$ at 4:30 p.m. 20/05, followed by a sharply decrease period (4:30 p.m. 20/05-1:00 a.m. 21/05), then gradually leveled off at an emission level of $\sim 0.020 \ \mu g \ cm^{-2} \ min^{-1}$. Deferring markedly from the sub-surface fertilization case, the effect of meteorological conditions on J_{NH_3} for the surface fertilization is quite obvious. The first rapid J_{NH_3} increase is likely triggered by the 6 mm precipitation, the second upsurge in J_{NH_3} might be associated with the raised temperature during daylight, the observed sharp decrease in J_{NH_3} could be attributed to the absence of sunlight and dropped temperature, while J_{NH_2} leveled off during the 3rd deployment day could be due to the applied urea being partially infiltrated into the surrounding soil facilitated by the relatively high soil water contents. The measured loss on the applied fertilizer *via* ammonia emission is found to be 11.87 kg N ha⁻¹ $(25.46 \text{ kg urea ha}^{-1})$, equaling 15.4% loss of the applied urea, more than triple of the loss measured from the sub-surface fertilization. The above experiments exemplify that OC-GPMCP can be used as an effective and practically implementable analytical tool to meaningfully investigate the effect of meteorological conditions on soil ammonia emission, highly valuable to guide the agricultural fertilization practice.

The same set of pre-calibrated OC-GPMCPs were deployed to the

selected cattle farm over three different occasions corresponding to different meteorological conditions to exemplify the applicability for monitoring soil ammonia emissions from livestock farms. All deployments were carried out at the same location in the stockyard surrounding area (Fig. S4c) from 8 a.m. to 12 noon of the next day. The soil pH at the site was determined to be \sim 7.93.

Fig. 4 and S14 show the real-time determined $J_{NH_3} - t$ profiles during the three deployment periods by the deployed OC-GPMCPs together with the air temperature profile and rainfall record. These $J_{NH_3} - t$ profiles were derived from the corresponding $\sigma_{25} - t$ profiles shown in Fig. S15. The $J_{NH_3} - t$ profile shown in Fig. 4a was obtained by OC-GPMCP#1 over a deployment period (8:00 a.m. 10/12–12 noon December 11, 2019) that was sunny during daylight, cloudless during the night and seven consecutive days without any rainfall prior to the deployment. During the deployment, the air temperature was varied between 23.8 and 29.5 °C. As can be seen, under such meteorological conditions, the observed change in J_{NH_3} follows the same trend as that of the temperature change, which can be further demonstrated by the J_{NH_3} – *t* profiles recorded over the same deployment period at the deployment locations of OC-GPMCP#2 and #3 (Fig. S14a). In fact, the correlation coefficients (*R*) derived from the J_{NH_3} – *Temperature* (*T*) plots (Fig. S16a-c) for OC-GPMCP#1, #2 and #3 are 0.79, 0.71 and 0.70, respectively. These confirm that the ammonia emission rate from dry soil is largely dictated by temperature. The peak J_{NH_3} values of 0.0055, 0.0071 and 0.0059 µg cm⁻¹ min⁻¹ corresponding to the deployment locations of OC-GPMCP#1, #2 and #3 were determined.

The ammonia emission behaviors of wet soil were then investigated under two meteorological scenarios. Fig. 4b displays the $J_{NH_3} - t$ profile recorded by OC-GPMCP#1 for the first scenario, for which, the deployment period (8:00 a.m. 02/12–12 noon December 03, 2019) was sunny during daylight and cloudless during the night, but several moderate rainfall events (a total precipitation of 13.2 mm) were recorded the day before the deployment. Interestingly, the influence of temperature on J_{NH_3} unveiled by the obtained $J_{NH_3} - t$ profile is almost identical to that obtained from the case of dry soil. Very similar ammonia emission behaviors can also be observed from the $J_{NH_3} - t$



Fig. 4. $J_{NH3} - t$ profiles obtained by OC-GPMCP#1 from the cattle farm under different meteorological conditions with air temperature profile and rainfall record. (a) Dry condition (8:00 a.m. 10/12–12 noon December 11, 2019); (b) After moderate rainfalls (8:00 a.m. 02/12–12 noon December 03, 2019); (c) After heavy storm (8:00 a.m. 25/12–12 noon December 26, 2019). The grey shields indicate night-time. The presented $J_{NH3} - t$ profiles are derived from the corresponding $\sigma_{25} - t$ profiles shown in Fig. S15.

profiles recorded by OC-GPMCP#2 and #3 during the same deployment period (Fig. S14b). The R values derived from the J_{NH_2} – T plots (Fig. S16d-f) are 0.80, 0.95, and 0.88, respectively, signifying a highly correlated $J_{NH_3} - T$ relationship. The peak J_{NH_3} values of 0.0549, 0.0651, and 0.0728 μ g cm⁻¹ min⁻¹ corresponding to the deployment locations of OC-GPMCP#1, #2 and #3 were determined. These peak J_{NH_2} values are much higher than those obtained from the dry soil, which could be due to the promoted decomposition of animal manures under wet and elevated temperature conditions (Häni et al., 2016; Saunders et al., 2012). For the second meteorological scenario, during the deployment period (8:00 a.m. 25/12-12 noon December 26, 2019), the weather was cloudy with several moderate rainfall events (Total precipitation: 11.6 mm), and one heavy storm with several moderate rainfall events (Total precipitation: 35 mm) were recorded within 12 h before the deployment (Fig. 4c and S14c). A period of sharp decrease in J_{NH_3} immediately after every moderate rainfall event is clearly observable, indicating that the ammonia emission behaviors are largely dictated by the moderate rainfall events rather than temperature, which contrasts strongly to the first scenario. The R values derived from the corresponding $J_{NH_3} - T$ plots (Fig. S16g-i) are -0.33, -0.37, and -0.26, respectively, categorically confirming a negatively correlated $J_{NH_3} - T$ relationship. This could be attributed to the precipitation induced high water content in surface soil that dissolves the surface soil ammonia and brings the dissolved ammonia to sub-surface soil through infiltration. The peak J_{NH_3} values of 0.0247, 0.0153, and 0.0336 μg cm⁻¹ min⁻¹ corresponding to the deployment locations of OC-GPMCP#1, #2, and #3 were determined, which are significantly lower than those obtained from the first meteorological scenario. This is likely due to the animal manure runoff and the saturation of water in soil caused by the heavy storm. The former decreases the available animal manures for ammonia generation via decomposition and the latter dilutes the surface soil ammonia content. These results exemplify that OC-GPMCP can be readily implemented to obtain real-time ammonia emission profiles for meaningful investigating the effect of meteorological conditions on ammonia emission from livestock farms.

4. Conclusions

In summary, the obtained results in this work exemplify the realworld applicability of OC-GPMCP to real-time continuously monitoring soil ammonia emissions in a simple and maintenance-free fashion. The recorded $J_{NH_3} - t$ profiles can be used to meaningfully correlate the soil ammonia emission behaviors with fertilization and meteorological conditions. The reported sensing system in this work provides an effective analytical tool for the researchers in environmental and agricultural fields to conduct large-scale soil ammonia emission assessments and gain scientific insights into the influence of fertilization/meteorological conditions on soil ammonia emission behaviors, critically important to mitigate soil ammonia emissions into the atmosphere and improve agricultural fertilization practice.

CRediT author statement

Ming Zhou: Conceptualization, Methodology, System development, Software, Data curation, Original draft preparation. Tianling Li: Assist in on-site system performance tests. **Porun Liu:** Writing - editing & proofreading. **Shanqing Zhang:** Conceptualization, Methodology. **Taicheng A** and **Huijun Zhao:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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