Membrane-based Conductivity Probe for Real-time In-situ Monitoring Rice Field Ammonia Volatilization

Tianling Li^{a,b}, Ming Zhou^a, Yuan Qiu^{a,c}, Jianyin Huang^{a,d}, Yonghong Wu^e, Shanqing Zhang^{a,}, Huijun Zhao^{a,*}*

^a Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, QLD 4222, Australia

^b Collaborative Innovation Centre of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, Jiangsu 210044, P. R. China

^c Guangxi Vocational and Technical Institute of Industry, 37 Xiuling Road, Nanning, Guangxi, 530005, P. R. China

^d Division of Information Technology, Engineering and Environment, School of Natural and Built Environment, Mason Lakes Campus, University of South Australia, Adelaide, SA 5095, Australia

^e State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, 71 East Beijing Road, Nanjing, Jiangsu 210008, P. R. China

*Corresponding Author

Prof. Huijun Zhao, Tel: +61-7-55528261, Fax: +61-7-55528067, E-mail: h.zhao@griffith.edu.au

Prof. Shanqing Zhang, Tel: +61-7-55528155, Fax: +61-7-55528067, E-mail: s.zhang@griffith.edu.au

Graphical abstract

Highlights

- ✓ Membrane-based electrochemical trace gas sensor
- ✓ Field-based ammonia real-time monitoring technique
- ✓ A effective technique to real-time track ammonia volatilization and evaluate environmental impact

Abstract

Reliable real-time and *in-situ* monitoring of ammonia volatilization could provide invaluable information in improving agriculture ammonia fertilizer utilization efficiency and solving ammonia relevant environmental issues, however, few applicable monitoring techniques are available in the current market. This work reported a new gaseous ammonia sensing principle and developed a gas-permeable membrane-based conductivity probe (GPMCP) to obtain critical information that enables insightful understanding of agriculture ammonia volatilization process. The analytical principle based on real-time measurement of the rate of conductivity increment in the receiving solution to achieve real-time, *in-situ* gaseous ammonia concentration and volatilization flux in a reliable and continuous fashion. It is also capable of obtaining an average ammonia volatilization flux and amount over a deployment period. The delicate design of GPMCP and developed precalibration strategy in this study bestows this technique a direct method that can effectively avoid ongoing calibration. Field deployments results showed that GPMCP had significant advantages on presenting continuous detailed ammonia volatilization information. The reported GPMCP can be an effective tool to monitor agricultural ammonia volatilization process.

Keywords: Membrane-based gas sensor; ammonia probe; *in-situ* real-time monitoring; soil ammonia volatilization

1 Introduction

The United Nations Food and Agriculture Organization predicts a world population growth to 9.15 billion by 2050, leading to a 70% increased demand for food [1]. This will undoubtedly accelerate the fertilizer consumption, driving up the fertilizer production [2, 3]. As an energy and resource intensive industry, fertilizer production accounts for ~1.2% of the world's energy consumption, of which ca. 93% is consumed to produce ammonia fertilizer [4, 5]. However,

only less than 40% of the applied ammonia fertilizer is effectively utilized by crops [6, 7]. The unused fertilizers are leached into soil and water bodies or volatilized into atmosphere, causing serious environmental problems (e.g., soil acidification, water eutrophication and fog haze), health issues (e.g., respiratory related diseases) and substantial economic and energy loss [8-13]. Therefore, improving ammonia fertilizer utilization efficiency is critically important for the green and sustainable agriculture practice. To achieve this, insightful understanding of the effect of key agriculture environmental parameters on ammonia volatilization (AV) process is a necessity; however, progress has been slow due mainly to the lack of effective and efficient monitoring techniques. It is envisaged that a reliable real-time *in-situ* gaseous ammonia monitoring technique can provide a powerful means to obtain valuable insights of agriculture ammonia volatilization (AAV) process.

Currently, AV is measured by indirect and direct methods [14]. The micro-plots based methods is a typical type of indirect methods that obtain the volatilized ammonia by deducting the measured amounts of plant uptake, soil residue and leaching loss from the total amount of the applied fertilizer using a micro-plot [15]. The results obtained by these indirect methods are unreliable due to the neglected microbial activities (e.g., soil denitrification) [16, 17]. Besides the complex, time-consuming and costly nature, such indirect methods are incapable of providing the required real-time respondent changes of AV flux (F_{AV}) to incidental environmental condition changes (e.g., temperature, soil moisture and air humidity) to meaningfully study AAV process.

The direct type of AV measurement methods currently in use can be classified into micro-meteorological and chamber based methods [16]. The former includes methods based on measuring mass balance, gradient diffusion, vorticity correlation and equilibrium concentration. Briefly, the mass balance method measures the horizontal ammonia flux on different planes to calculate F_{AV} [18, 19], the gradient diffusion method utilizes the turbulent diffusion coefficient

and ammonia concentration gradient to deduce F_{AV} [18, 20]; the vorticity correlation method relies on the vertical wind speed pulsation and ammonia concentration pulsation to obtain F_{AV} [21, 22]; the equilibrium concentration method obtains F_{AV} from the difference in the ammonia concentration and diffusion impedance between soil and air [23]. The open air *in-situ* monitoring is a greatest advantage of such micro-meteorological methods as it enables the monitoring to be directly carried out under the natural environment. However, all of these methods require to determine ammonia concentration, mostly by laboratory-based optical analysis methods (e.g., the absorption or luminescence intensity changes at a fixed wavelength proportional to ammonia concentration). These methods also require considerable technological input, large testing soil area (e.g. radius of 15 - 40 m) and relatively homogenous meteorological conditions [24, 25]. The chamber based methods have been widely used in AV monitoring that include closed-chamber, wind tunnel and ventilated-chamber methods. The closed-chamber method measures F_{AV} in a closed space, where environment conditions (e.g., pressure, temperature, humidity and wind speed) could differ from real environment, leading to overestimated or underestimated results, especially during weather changes such as rain or wind [26]. The wind tunnel method makes up the shortcomings of the closed-chamber by pumping air through the chamber [27], but the drawbacks of high costs and difficulties in determining the optimal tunnel size to achieve accurate results have limited its widespread application [28, 29]. The ventilated-chamber method usually employs sponge-soaked phosphoric acid glycerine to absorb the volatilized ammonia in a ventilative tube and extracted by potassium chloride. Noticeable advantages of the method are its simple device structure and low-cost. However, the method possesses low sensitivity and its measurement results can be seriously compromised by the manual operation [30, 31]. Although some chamber based methods have been successfully used to monitor AV [32-34], these methods are unable to real-time monitor AV process with necessary temporal resolution as they are essentially *in-situ*

sampling methods rather than detection methods, and requiring laboratory analysis to determine ammonia concentration to calculate F_{AV} . Therefore, there is a prominent need to develop new analytical techniques capable of continuously *in-situ* monitoring AAV process in real-time and with high temporal resolution [35].

We recently reported a simple gas permeable membrane based conductivity probe (GPMCP) technique and successfully applied to *in-situ* continuously monitor the dissolved ammonia in aquatic environment in real-time and with high temporal resolution [36]. In this work, a new gaseous ammonia detection principle was developed to empower the GPMCP for AV monitoring. Systematic experiments were carried out to validate the proposed gaseous ammonia detection principle. The feasibility of using the developed technique to monitor AAV process were demonstrated by rice field deployments. The obtained results demonstrated that the GPMCP embedded with the new gaseous ammonia detection principle can be used to *in-situ* continuously monitor F_{AV} in a real-time and high temporal resolution manner. The further development and widespread use of the reported GPMCP technique could foster a better understanding of AAV process, providing solid scientific basis to guide the development of efficient fertilizer utilisation strategy.

2 Materials and methods

2.1 Chemicals and materials

All chemicals were of analytical reagent grade and purchased from Merck, unless otherwise stated. All solutions were prepared by deionised water (Millipore Corp., 18 M Ω cm). PTFE membranes (FluoroporeTM, pore size: 0.22 μ m, porosity: 85%, diameter: 47 mm, thickness: 150 μ m) are purchased from Merck and employed as the gas permeable membrane. Conductivity meter (Model 3084, Amber Science, Oregon, USA and pH meter (Mettler-Toledo AG, Switzerland) was used to calibrate the conductivity probe in GPMCP.

2.2 GPMCP assembly and sensing system set-up

Figure 1a shows GPMCP configuration. The details can be found from our previous report [36].

Figure S1 shows a typical laboratory sensing system setup. A 9.0 L sealed sample tank filling with 4.0 L of solution containing different concentrations of NH_4Cl was used for all laboratory validation experiments. Two GPMCPs with temperature sensor were fixed 2 cm above the solution level. In order to fully convert NH_4^+ into NH_3 , under constant stirring, 1.0 mL of 10 M NaOH was added to ensure the solution $\text{pH} > 12$. A pH sensor was deployed in the solution to monitor solution pH. All experiments were carried out in a constant temperature room/chamber. For each NH_4Cl concentration, gas samples were collected from the sample tank 5 min after adding NaOH. The collected gas samples were absorbed by 0.010 M H_2SO_4 and analyzed by standard colorimetric method (APHA 4500- NH_3) [37]. Two GPMCPs were also deployed in the sample tank to real-time monitoring the ammonia concentration in solution. GPMCP took conductivity readings every 10 s and recorded an average reading every minute. Data generated by temperature and pH sensors were recorded every minute. The data recorded by all sensors were recorded by a home-made multichannel data logger/sensor controller and real-time transferred a computer through a wireless receiver.

2.3 Field deployment

All field deployments were carried out using a self-powered data logger (Figure S2) that can hold up to 8 GPMCPs, 1 temperature and 1 pH sensor continuously operate during deployment period. The data logger was remotely controlled by a computer. Figure S3 schematically illustrates the field deployment of the GPMCPs. The recorded temperature was used for the data corrections.

Two rice fields (Site #1 and Site #2) were selected to deploy the developed GPMCPs. Both sites are located at Hefei, Anhui, China. Two GPMCPs were deployed in these sites, hanging

above the water level (ca. 2 cm), and each site covers an area of 0.03 m² (Figure S3). The water pHs in Site #1 and Site #2 are 7.2-7.4 and 7.9-8.2, respectively. During a 3-day experimental period, both sites were continuously monitored for the first 24 hours to obtain the blank, followed by applying 0.25 g NH₄Cl to each site at 24th and 48th hours, respectively.

3 Results and discussion

3.1 Detection principle

Figure 1b schematically illustrates the gas phase ammonia ($\{NH_3\}_g$) detection principle of GPMCP. When a GPMCP is deployed in a sample, $\{NH_3\}_g$ will rapidly diffuse to the outer membrane interface, permeate through the membrane and react with boric acid at the inner membrane interface (Eq. 1).

The transport of $\{NH_3\}_g$ across GPM is driven by the ammonia partial pressure differences ($dP = P_{NH_3} - P'_{NH_3}$) between the outer and inner membrane interfaces. This differs markedly from the detection of the dissolved ammonia ($\{NH_3\}_{aq}$) in aqueous sample, where the permeation through the membrane is controlled by the phase transformation of $\{NH_3\}_{aq}$ into $\{NH_3\}_g$ at the outer membrane surface [36]. Because of the rapidity of the acid–base reaction, the permeated $\{NH_3\}_g$ will be instantly consumed by the boric acid at the inner membrane interface *via* Eq. 1, creating an essentially zero ammonia partial pressure condition ($P'_{NH_3} \approx 0$) at the inner membrane interface. Also, for analytical conditions used in this work, the ammonia partial pressures at the outer membrane interface are very low. The P_{NH_3} can therefore be converted into molarity concentration in accordance with the ideal gas equation (Eq. 2).

$$dp = (P_{NH_3} - P'_{NH_3}) = P_{NH_3} = RT \cdot [NH_3]_g \quad (2).$$

Where, $[NH_3]_g$ is the gas phase ammonia concentration, R and T are the ideal gas constant and absolute temperature, respectively. Because $\{NH_3\}_g$ transport across the membrane is directly proportional to the ammonia partial pressure differences (dP), the instantaneous flux (J_{NH_3}) of ammonia permeating through the membrane can therefore be expressed as:

$$J_{NH_3} = \frac{d(N_{NH_3})}{dt \cdot S} = k \cdot dp = k \cdot RT [NH_3]_g \quad (3).$$

Where, N_{NH_3} refers to the number of moles of permeated ammonia, S is the exposed area of membrane (fixed at 7.07 cm^2 for all GPMCPs used in this study), and k is the proportional constant that depends on the characteristics of the membrane. It is to note that in effect, the measured J_{NH_3} is the instantaneous rate of ammonia volatilization (F_{AV}).

As the permeated $\{NH_3\}_g$ is stoichiometrically converted into NH_4^+ via Eq. 1, the rate of NH_4^+ concentration increase in the receiving phase can therefore be expressed as:

$$\frac{d([NH_4^+])}{dt} = \frac{S \cdot J_{NH_3}}{V_R} = \frac{S \cdot kRT [NH_3]_g}{V_R} \quad (4).$$

Where, V_R is the volume of the boric acid receiving phase. Considering the rate of the receiving phase conductivity increase (R_{CI}) is directly proportional to the rate of the receiving phase NH_4^+ concentration increase, R_{CI} can be presented as:

$$R_{CI} = \frac{d\sigma}{dt} = \rho \frac{d([NH_4^+])}{dt} = \rho \frac{S \cdot kRT [NH_3]_g}{V_R} = K_I [NH_3]_g \quad (5a)$$

$$R_{CI} = \frac{d\sigma}{dt} = \rho \frac{S \cdot J_{NH_3}}{V_R} = K_2 J_{NH_3} \quad (5b).$$

Where, ρ is the proportional constant of the embedded EC detector in a GPMCP, K_I (denoted as the concentration constant) and K_2 (denoted as the flux constant) are the probe constants of a given GPMCP for ammonia concentration and flux measurements, respectively. It should be noted that ρ , K_I and K_2 are experimentally determined. Eqs. 5a and b indicate that the instantaneous $\{NH_3\}_g$ concentration ($[NH_3]_g$) and flux (J_{NH_3}) can be determined by measuring

R_{CI} of the boric acid receiving phase. Furthermore, the average ammonia concentration ($\overline{[NH_3]_g}$) and flux ($\overline{J_{NH_3}}$) over a given deployment period of t can be determined by:

$$\overline{[NH_3]_g} = \frac{R_{CI}}{K_1} \quad (6a)$$

$$\overline{J_{NH_3}} = \frac{R_{CI}}{K_2} \quad (6b)$$

Considering $\int_0^t ([NH_3]_g) dt$ and $\int_0^t (J_{NH_3}) dt$ are the integration of instantaneous sample ammonia concentration and flux over an entire deployment period, respectively, the determined $\overline{[NH_3]_g}$ and $\overline{J_{NH_3}}$ by Eqs. 6a and b should be regarded as an absolute average ammonia concentration and ammonia volatilization flux.

3.2 Validation of detection principle

The proposed detection principle was initially validated under well-controlled analytical environment using NH_4Cl solution generated gaseous ammonia in a sealed sample tank. All validation experiments were carried out in a constant temperature room at $25^\circ C$. $[NH_3]_g$ and $[NH_3]_{aq}$ relationships for solutions containing different NH_4Cl concentrations were firstly determined. A linear relationship was obtained (Figure S4) and used to guide the generation of different $[NH_3]_g$ for detection principle validation and probe calibration. The time required to achieve steady $[NH_3]_g$ with different NH_4Cl concentrations was also determined (Figure S5). It was found that for all cases investigated, $[NH_3]_g$ becomes constant 5 min after NaOH was added to bring NH_4Cl solution pH >12 to fully convert NH_4^+ into dissolved NH_3 (i.e., $[NH_4^+] \approx [NH_3]_{aq}$). On this basis, gas samples were taken from the sample tank every 5 min after NaOH was added and the $[NH_3]_g$ values of the collected gas samples were determined by standard colorimetric method [37]. Also, GPMCP starts recording data 5 min after NaOH was added. Figure S6 shows the relationship between the measured $[NH_3]_g$ and $[NH_4^+]$ in receiving solution ($[NH_4^+]_R$), which is used to convert the measured $[NH_3]_g$ to J_{NH_3} in this study.

Figures 2a and 2b show a set of original GPMCP conductivity response (σ) – deployment time (t) curves reordered under different $[NH_3]_g$. Excellent linear relationships were observed for all cases investigated. Therefore, for each $[NH_3]_g$, the rate of receiving phase conductivity increase (R_{CI}) can be derived from the slope of the corresponding $\sigma - t$ curve. For a given GPMCP and temperature, Eq. 5a and 5b predict a linear relationship between R_{CI} and $[NH_3]_g$, and R_{CI} and J_{NH_3} , respectively. Figure 2c shows a plot of R_{CI} against $[NH_3]_g$. A linear line with $R^2 = 0.997$ was obtained, signifying the validity of Eq. 5a. The probe concentration constant (K_1) of the GPMCP can be obtained from the slope of the $R_{CI} - [NH_3]_g$ curve. At 25°C, $K_1 (25^\circ\text{C}) = 0.167 \mu\text{S cm}^{-1} \text{ min}^{-1} \mu\text{g}^{-1} \text{ L}$. In fact, K_1 also defines the probe sensitivity. Under the experimental conditions, the presence of $1 \mu\text{g L}^{-1}$ ammonia will lead to $0.167 \mu\text{S cm}^{-1}$ increase within a minute. As such, the detection limit of GPMCP will be increased with the deployment time because the analytical signal (σ) used to quantify the ammonia concentration by GPMCP has accumulative nature. Figure 2d demonstrates a linear relationship between R_{CI} and J_{NH_3} with $R^2 = 0.995$ (derived from Figures 2a, 2b and S6), which confirms the validity of Eq. 5b. The ammonia flux constant (K_2 in Eq. 5b) can be determined from the slope of $R_{CI} - J_{NH_3}$ plot. At 25°C, $K_2 (25^\circ\text{C}) = 10.65 \mu\text{S cm} \mu\text{g}^{-1}$.

In order to validate Eq. 6a and 6b, the same GPMCP was used to obtain a set of $\sigma - t$ curves from different $[NH_3]_g$ under 25°C (Figure 3a). Based on the obtained R_{CI} from Figure 3a and $K_1(25^\circ\text{C}) = 0.167 \mu\text{S cm}^{-1} \text{ min}^{-1} \mu\text{g}^{-1} \text{ L}$, $\overline{[NH_3]}_g$ for corresponding $\sigma - t$ curves over the deployment period were determined by Eq. 6a and shown in Figure 3b. The obtained results demonstrate that GPMCP is capable of determine the average ammonia concentration over a given deployment period, providing useful information to understand AAV process [38]. Figure 3c reveals a linear relationship ($R^2 = 0.993$) between $\overline{[NH_3]}_{\text{GPMCP}}$ and $\overline{[NH_3]}_{\text{STD}}$ with a slope value of 0.961. The near unity slope value suggests that $[NH_3]_g$ determined by both

methods are essentially the same. Figure 3d shows the $\overline{J_{NH_3}}$ determined by Eq. 6b over the corresponding deployment periods shown in Figure 3a, demonstrating the capability of GPMCP to track $\overline{J_{NH_3}}$, highly valuable for studying AAV process.

The selectivity is one of the most important performance parameter of any analytical method, especially important for field-based analytical methods. In this regard, GPMCP is designed to possess high selectivity. As confirmed in our previous report [36], the combined effect of the gas permeable membrane and the acidic receiving phase employed in GPMCP can effectively eliminate potential interferences from all none-gaseous species and acidic gaseous species. In principle, GPMCP can only respond to alkaline gases. Considering the vast majority of atmospheric gaseous species are neutral species (i.e., O₂, N₂, etc.) and acidic species (i.e., CO₂, H₂S, SO₂, etc.), while ammonia is the only atmospheric alkaline gas with appreciable concentrations, the determination of gaseous ammonia by GPMCP can be claimed as “specific”.

3.3 Probe calibration

The above results validated the proposed detection principle under a fixed temperature of 25°C. However, for a given GPMCP, Eq. 5a and 5b suggests that the EC constant ρ , and probe concentration constant K_I are temperature dependent. K_2 should be independent of temperature on the basis that ρ has been calibrated for temperature. This means that for practical use, both ρ and K_I need to be corrected for temperature induced changes. In this work, the embedded temperature sensor is used to real-time determine the receiving phase temperature for probe calibration.

The temperature correction of the embedded EC detector was conducted by determining conductivity changes of 0.500 M boric acid receiving phase under different temperatures (T, °C). A linear $\sigma - T$ relationship was obtained from GPMCP#1 with slope and intercept values of 1.19 $\mu\text{S cm}^{-1} \text{ } ^\circ\text{C}^{-1}$ and 22.9 $\mu\text{S cm}^{-1}$, respectively (Figure S7). Therefore, for GPMCP#1, the

measured σ_T under a given temperature (T , °C) can be converted to a ‘standard’ conductivity value at 25°C (σ_{25}) by:

$$\sigma_{25} = \sigma_T + 1.19 \times (25 - T) \quad (7).$$

It is to note that the temperature in Eq. 7 is the receiving phase temperature that can be real-time determined by the embedded temperature sensor. It is also to note that in this work, all measured conductivity data have been automatically converted into σ_{25} using the temperature correction formula shown in Eq. 7 by the sensor control software.

The temperature correction of the probe concentration constant K_I was carried out. Figure S8 shows 6 groups of $\sigma - t$ and corresponding $R_{CI} - [NH_3]_g$ curves determined by GPMCP under different temperatures between 19.8 and 44.8°C. Each group of $\sigma - t$ curves is measured under a constant temperature from a set of $[NH_3]_g$ and used to obtain R_{CI} values. The determining the slope from a $R_{CI} - [NH_3]_g$ curve is the $K_I(T)$ value of the probe under the temperature. The probe constant and temperature dependent relationship can then be determined by plotting $K_I(T)$ against T (Figure 4a). For GPMCP#1, the obtained simple linear relationship can be mathematically expressed as:

$$K_I(T) = 0.00634T(^\circ\text{C}) + 0.00674 \quad (8).$$

This means that the probe constants of different temperatures can be readily obtained by simply substitute the corresponding temperature into Eq. 8. It must be noted that the temperature shown in Eq. 8 is the gas phase sample temperature rather than the temperature of the receiving phase. Therefore, a temperature sensor needs to be deployed in gas phase to obtain data for K_I correction. Similarly, the determined slope from a $R_{CI} - J_{NH_3}$ curve is the $K_2(T)$ value of the probe under the given temperature (Figure S9). The relationship between K_2 and temperature is illustrated in Figure 4b. As aforementioned, K_2 is essentially independent of temperature once the EC constant ρ is corrected for temperature (i.e., convert the measured σ_T to σ_{25}). For GPMCP#1, $K_2(T) = 10.65 \mu\text{S cm } \mu\text{g}^{-1}$. It should be mentioned that once a GPMCP is calibrated

by the above described calibration, it does not require ongoing calibration, which is highly desirable for a field-based monitoring technique. Such an unique feature of GPMCP is advantageous to reduce operational and maintenance costs, and achieve high reliability [39, 40].

The stability is an important performance indicator for field-based sensing systems. Unfortunately, we could not directly evaluate the long-term stability of GPMCP due to the following practical difficulties: (1) Due to accumulative nature, with the currently employed membrane size, receiving phase volume and conductivity measurement capability by GPMCP, a higher ammonia concentration (e.g., $10 \mu\text{g L}^{-1}$) will increase the receiving phase conductivity within 20 h to a value exceeded the conductivity measurement limit of $2000 \mu\text{S cm}^{-1}$; (2) it is very difficult to retain a detection environment with a constant gaseous ammonia concentration over a long period. Therefore, the reliability experiments were performed to evaluate the practicality of GPMCP for continuous monitoring applications. Figure S10 shows a set of $\sigma - t$ curves obtained by CPMCP#1 over a period of 55 days. During each deployment, a given NH_4Cl concentration solution in a sealed sample tank was used to generate $1.30 \mu\text{g L}^{-1} \{\text{NH}_3\}_g$ (confirmed by the standard method). It should be noted that over the test period, other than obtaining the results shown in Figure S10, the GPMCP was also used for various other experiments without additional calibration. The determined $[\overline{\text{NH}_3}]_g$ values from Figure S10 in according to Equations 6a and b with $K_I = 0.167 \mu\text{S cm}^{-1} \text{ min}^{-1} \mu\text{g}^{-1} \text{ L}$ are almost unchanged over the test period. Also, the GPMCP determined $[\overline{\text{NH}_3}]_g$ is very close to those determined by the standard method within a range of $1.30 \pm 0.19 \mu\text{g L}^{-1}$. These results confirm that when the accumulated conductivity in the receiving phase is below the measurement capability, GPMCP can be reliably used to continuously monitor gas phase ammonia.

3.4 Field deployment

GPMCPs were deployed at two rice field sites to real-time monitoring AV. GPMCP#1 (see Table S1, $\sigma_{25} = \sigma_T + 1.19 \times (25 - T)$; $K_1(T) = 0.00634T(^{\circ}\text{C}) + 0.00674$; $K_2 = 10.65 \mu\text{S cm } \mu\text{g}^{-1}$) was deployed at Site #1. Figure 5a shows the real-time recorded temperature, conductivity, AV concentration and flux over the deployment period. A minimal volatilized ammonia was detected before fertilization. Sharp AV can be determined almost immediately after fertilization. It was found that both volatilized ammonia concentration and instantaneous AV flux are varied with the daily temperature changes. An increased temperature results in an increase for both volatilized ammonia concentration and instantaneous AV flux (Figures 5b). The average volatilized ammonia concentrations after 1st and 2nd fertilization are found to be 0.88 and 1.88 $\mu\text{g L}^{-1}$, respectively. Also, the average AV flux after 1st and 2nd fertilization are found to be 0.06 and 0.14 $\text{kg N hm}^{-2} \text{ h}^{-1}$, respectively. Moreover, the total fertilizer loss in the deployed area after 1st and 2nd fertilization are calculated to be 4.12 and 9.26 mg of ammonia nitrogen, respectively. This means that 6.3% and 7.3% of the applied fertilizer are volatilized during 1st and 2nd fertilization periods, respectively. These results also suggest that a larger amount of applied fertilizer leads to a higher volatilization loss of fertilizer. The relationship between pH and the AV flux was also investigated (Figure 5c). Although only small pH changes (resulting from the fertilization actions) were observed over the deployment period, it confirms that a higher pH leads to a higher AV flux, consistent with the theoretical prediction and previous studies [41, 42].

GPMCP#2 (see Table S1, $\sigma_{25} = \sigma_T + 1.17 \times (25 - T)$; $K_1(T) = 0.00620T(^{\circ}\text{C}) + 0.00580$, $K_2 = 10.58 \mu\text{S cm } \mu\text{g}^{-1}$) was deployed at Site #2 and the obtained data are shown in Figure S11. The observed AV behaviors are similar to those observed from Site #1; however, the volatilized ammonia concentrations and the volatilization fluxes are higher due to higher pH. The measured average volatilized ammonia concentration after 1st and 2nd fertilizations are 2.30 and

2.55 $\mu\text{g L}^{-1}$, respectively, corresponding to 15.6% and 10.5% fertilizer loss, respectively. It worth to note that the lower fertilizer loss after 2nd fertilization is due to the change of fertilization method where a deep-fertilization was used to replace the surface fertilization. This also implies that the fertilization method plays an important role to minimize the fertilizer loss via volatilization. The results obtained from the rice field deployments demonstrated the applicability of the developed method for monitoring the agriculture ammonia volatilization process. The reported GPMCP can be adapted/further developed for real-time monitoring other agriculture ammonia volatilization processes.

4 Conclusion

In summary, we proposed and experimentally validated a gas phase ammonia detection principle that is capable of *in situ*, real-time continuously monitoring ammonia volatilization process. The results obtained from the rice field deployments demonstrated the applicability of the developed method for monitoring the agriculture ammonia volatilization process. The reported GPMCP can be adapted/further developed for real-time monitoring other agriculture ammonia volatilization processes.

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Appendix A. Supplementary data

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Figure Captions

Figure 1. (a) Schematic diagram of GPMCP configuration; (b) Conceptual view of gas phase ammonia sensing principle

Figure 2. (a) (b) Reordered $\sigma - t$ profiles under different $[NH_3]_g$ ranged from 0.0106 to 20.2 $\mu\text{g L}^{-1}$; (c) $R_{CI} - [NH_3]_g$ relationship derived from Figures 2a and 2b; (d) $R_{CI} - J_{NH_3}$ relationship derived from Figures 2a, 2b and S6. All the experiments were carried out at 25°C

Figure 3. (a) Recorded $\sigma - t$ profiles from successively increased $[NH_3]_g$; (b) $\overline{[NH_3]}$ determined by Eq. 6a; (c) Correlation relationship between $\{NH_3\}_g$, concentrations measured by GPMCP ($[NH_3]_{\text{GPMCP}}$) and standard method ($[NH_3]_{\text{STD}}$); (d) $\overline{J_{NH_3}}$ determined by Eq. 6b

Figure 4. (a) Temperature correction for K_I of GPMCP#1 (Data are derived from Figure S8); (b) K_2 – temperature relationship for GPMCP#1 (Data are derived from Figure S9)

Figure 5. (a) Recorded temperature, σ , $[NH_3]_g$, J_{NH_3} and time profiles from Site #1; (b) Temperature and J_{NH_3} relationships during 1st and 2nd fertilizations; (c) pH and J_{NH_3} during 1st and 2nd fertilizations

(a)

(b)

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