



In situ visualization of soil profile acidification and processes following nitrogen fertilization and liming

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ABSTRACT

Soil pH is the master variable of soil properties and understanding its spatiotemporal changes *in situ* is key to unveiling numerous biogeochemical processes. The development of non-invasive imaging techniques provides the possibility to visualize and localize soil pH changes depending on various factors, e.g. fertilization and climate. Herein, the optodes pH mapping system was used to study the effects of eight fertilizer types including chicken manure, $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, KNO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and urea on the spatiotemporal distribution of soil pH with and without liming at 10 °C and 25 °C. Ammonium-based fertilizers, especially NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and $\text{NH}_4\text{H}_2\text{PO}_4$ strongly decreased soil pH by a maximum of 1.4 ± 0.16 units at both temperatures. The 0–2 cm, where fertilizers were applied, had the highest pH decreases, from where the acidity rapidly diffused to depth. The acidified depth extended down to 4.5 ± 0.14 cm over 60 d. Chicken manure increased the pH within 5 d, but the pH decreased again after 60 d. Soil temperature was a strong controller of acidity generation and transport to depth after fertilization: pH decreased by 0.1 ± 0.07 – 0.3 ± 0.07 units more at 25 °C than 10 °C due to increased activity of nitrifying microorganisms, and higher temperature accelerated the spatiotemporal dynamics of soil acidity. Although pH increased shortly after liming compared to unlimed soils, it decreased after adding ammonium-based fertilizers. Therefore, N fertilizer types and temperature should be considered for having a more efficient fertilization management with less consequences for soil acidification. The planar optode is a powerful non-invasive imaging technique that enables *in situ* visualization of the spatiotemporal changes of soil pH profile after fertilization.

1. Introduction

Nitrogen (N) fertilizers play a crucial role in increasing crop yields and safeguarding the food demand of the global human population (Cai et al., 2023). The excessive N and the lower N use efficiency lead to intensive soil acidification since the 1980s (Li et al., 2019; Tao et al., 2019; He et al., 2021; Zhu et al., 2023a). For example, the average soil pH value of croplands in China decreased by 0.13–0.76 units (Guo et al., 2010). Soil acidification increases the availability of metal ions such as aluminium, lead, and cadmium in soil solution, which are toxic to plants and directly threaten food production (Xing et al., 2022) or increase the

vulnerability of plants to diseases, for example leading to root rot (Li et al., 2023a; Zamanian and Kuzyakov, 2022). Ultimately, soil acidification endangers soil health, biodiversity, terrestrial ecosystems and their functioning of services such as the inorganic carbon pool, organic carbon stability, microbial network complexity, soil fertility and health (Groshans et al., 2018; Kuzyakov et al., 2021; Právělie, 2021; Kerfahi et al., 2024).

The average H^+ produced by N fertilization accounted for 54 % of the total soil H^+ generated of croplands in south China (Xu et al., 2022). The number of protons produced in the soil depends on the type of the applied N fertilizers (Hao et al., 2020). Nitrification following the

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application of ammonium-based mineral fertilizers generates nitrate and proton ions, which can strongly acidify the soils if the nitrate ions are not fully taken up by the roots and release hydroxyl to compensate for proton ions (Zamanian et al., 2024). By contrast, the application of organic fertilizers may even increase soil pH by release of basic cations during decomposition. The relatively slow decomposition rate of organic compounds in particular increases the N uptake by the roots (Jia et al., 2022). Soil initial pH value, as well as environmental factors such as temperature and precipitation are considered as the main controllers of pH changes throughout of the soil profile, especially in response to N fertilizers (Ouyang et al., 2017; Li et al., 2019). In particular, the activity of nitrifying microorganisms and the mineralization rate of organic matter are sensitive to soil temperature (Zhao et al., 2022; Sun et al., 2023; Chen et al., 2024).

Soils are the most heterogeneous parts of the biosphere, with an extremely high differentiation of properties and processes from nano- to macro-scales (Kuzyakov and Blagodatskaya, 2015). The pH is the master variable of many soil properties and is generally measured in the laboratory by destructive sampling. This method cannot reflect the actual spatiotemporal distribution and changes in soil pH *in situ*. This is particularly important as soil pH changes control the vertical variation of other soil properties in response to land management. Therefore, focusing only on the surface soil pH biases our understanding about the effects of land management practices such as N fertilization on various soil properties throughout the soil profile (Chen et al., 2023). Clarifying the variations of soil pH with time and in response to environmental factors plays a determinant role in improving the N use efficiency and reducing soil acidification. In this regard, the *in situ* visualization of the spatiotemporal distribution of soil pH is a suitable approach, which can also unveil numerous biogeochemical processes that are controlled by the soil pH (Bilyera et al., 2020; Tian et al., 2020). A classical and successful method used to visualize pH value in the soil–root interface was developed in the early 1980s using bromocresol purple to map pH distribution by placing agarose gel on the soil–root interface (Marschner and Römhild, 1983; Jaillard et al., 1996). However, most of those studies are point measurements and have poor spatial or temporal resolution (Rudolph et al., 2013). In addition, only one measurement was possible and pH dynamics cannot be continuously observed *in situ* over time (Jaillard et al., 1996).

The developed planar optode provides a non-destructive technique that enables the *in situ* visualization and localization of pH changes in the soil (Merl et al., 2022). This is an excellent option for tracing soil acidification and clarifying the soil pH hotspots and intensities after N fertilization under changing environmental factors such as temperature. Previous studies have applied this method to various soil types, to analyse the effects of sludge or biochar on pH value, and O_2 and NH_3 content (Merl and Koren, 2020; Merl et al., 2022; Bornø et al., 2023; Merl et al., 2024). Although the effects of different N fertilizer types on soil pH has been investigated, such studies were limited to visualize the effects of only ammonium-based N fertilizers, urea or manure, within just three days after fertilization (Merl and Koren, 2020; Merl et al., 2024). Consequently, these studies didn't capture the long-term effects of soil buffering capacity and the environmental factors on the ultimate pH changes. Therefore, we used the planar optode technology provided by the 'optodes pH mapping system' (PreSens GmbH, Regensburg, Germany) to visualize the spatiotemporal variations in pH values in soil profiles following the application of N fertilizers within two months. The main objective was to reveal through visual illustration the actual soil pH profile and its spatiotemporal characteristics in relation to the following factors: (i) N fertilizer types, (ii) temperature, and (iii) liming. We hypothesized that (i) ammonium-based N fertilizers acidify a larger soil volume over comparatively shorter periods than nitrate-based and organic fertilizers. (ii) Relatively warmer temperatures during and after fertilization leads to stronger soil acidification.

2. Materials and methods

2.1. Soil collection and experimental setup

Soil samples were collected from an agricultural field in Göttingen, Germany. The climate is temperate oceanic. The mean annual temperature is 9.5°C, and the mean annual precipitation is 624 mm. The soil is classified as Stagnic Luvisol (WRB, 2014), and has a silt loam texture with a bulk density of 1.25 g cm⁻³. The water holding capacity (WHC) was 28 %, and the soil pH in 1:2.5 soil-to-water ratio was 7.4. The total organic C content was 10.4 g kg⁻¹, and the CaCO₃ content was 7.5 g kg⁻¹ soil. The soil was sampled at a depth of 0–20 cm of the plow layer using an auger. Five soil samples were mixed to form a composite. The sampled soil was air-dried and sieved through a 2 mm screen before the incubation experiment.

An incubation experiment was conducted for 60 d to study the effects of N fertilization and temperature on pH values and acidification rates in an eight-cm soil profile. The experiment included three factors: (i) the eight N fertilizer types were selected given their acidification potential due to different N sources as well the cations being present: ammonium sulfate ((NH₄)₂SO₄), ammonium dihydrogen phosphate (NH₄H₂PO₄), ammonium nitrate (NH₄NO₃), urea, potassium nitrate (KNO₃), calcium nitrite (Ca(NO₃)₂), magnesium nitrate (Mg(NO₃)₂), and chicken manure; (ii) two temperatures: 10°C and 25°C, the temperature level was set according to the annual average temperature and the average maximum temperature of the study region's climate. Thus, 18 treatments, including two of no N fertilizer at 10°C and 25°C, were arranged according to a completely randomized design. In order to further determine the effect of lime on rapid soil acidification caused by N fertilizers, we set (iii) two liming scenarios: with or without the addition of CaCO₃ (note that the effects of liming were considered only on soils that received KNO₃ and (NH₄)₂SO₄ as we expected the lowest and highest acidity productions, respectively, by these fertilizers). These consisted of 6 treatments, including two of no N fertilizer in the two liming scenarios, which were also arranged according to a completely randomized design. In the limed soils, where CaCO₃ powder was added, the CaCO₃ content of the soils increased from 7.5 to 20.5 g kg⁻¹ soil. Based on a bulk density of 1.25 g cm⁻³ at 8 cm soil, this corresponded to exogenous addition 13.3 t CaCO₃ ha⁻¹. The problem of low N utilization and excessive N fertilization in developing countries are serious, with some N fertilization exceeding 300 kg N ha⁻¹ (He et al., 2021). Therefore, in order to clarify the effect of excessive N fertilization on soil acidification, the amount of N added by each fertilizer type was 0.25 g N kg⁻¹ soil equal to 360 kg N ha⁻¹ (Table S1). In total, 24 treatments were conducted, including two control soils, i.e. soil without fertilization and liming (Contr-1) and soil without fertilization but with CaCO₃ addition (Contr-2). Each treatment had three replicates.

The 2 mm sieved soil was homogeneously filled into boxes (12 × 10 × 1.2 cm) to avoid layering and had a homogeneous bulk density of 1.25 g cm⁻³. CaCO₃ powder was homogeneously mixed with the soil in the limed treatment before filling the boxes. The soil moisture contents in all treatments were initially adjusted to 60 % of WHC using a 1 mL pipette before fertilization. The soils in boxes were pre-incubated for 7 d at 25°C to reactivate microbial activity (Paul et al., 2006; Raza et al., 2024a). Thereafter, dissolved N fertilizers were evenly applied on the soil surface in each box, ensuring that the final water content was 80 % of WHC. All boxes were kept in two climate chambers without light at 10°C and 25°C, respectively. To maintain the soil water content, boxes were checked regularly by weighing and the moisture deficit was compensated by watering from the top. During the incubation period, all boxes were placed with the openable side at an angle of ~45° to ensure a smooth surface for imaging (Li et al., 2007).

2.2. pH mapping by planar optode and measurement

Boxes were opened from one side 5, 12, 20, 40, and 60 d after

fertilization for pH imaging by the non-destructive method using the 'optodes pH mapping system' (PreSens GmbH, Regensburg, Germany). They allow 2D-sensing (imaging) of pH distribution. The optodes pH mapping system includes a PC, software (VisiSens AnalytiCal 2), a camera with detector (VisiSens TD), chemical optical pH sensor foils also called optodes (SF-HP5R with a pH range between 5.5 and 7.5) and LED light (excitation wavelength of 470 nm) (Blossfeld, 2013; Blossfeld et al., 2013; Ma et al., 2019). The chemical optical pH sensor foil has three layers: (1) an analyte-insensitive layer (125 μm thick), a layer of transparent polycarbonate support that is not responding to H^+/OH^- ; (2) an analyte-sensitive layer (20 μm thick) incorporating the fluorescent dyes and responding to the pH value; and (3) an optical isolation layer (20 μm thick) blocking ambient light, excluding interferences from the sample and not responding to the soil pH value. To prepare pH sensor foils, the foil was cut into 10×10 cm and the insensitive side of foils was attached to a semi-rigid transparent plastic film. The analyte-sensitive layer was directly attached to the soil surface of each box for 2 min to react under LED light (Fig. 1). The camera connected to a PC was used to detect the fluorescence signals changes due to the interaction of the indicator dye with H^+ or OH^- ions of the foil. The indicator dye is emitting green fluorescence signals that are changing dynamically with varying analyte concentration. The reference dye gives a stable and constant light signal. These emissions from indicator and reference meet exactly the red and green channel sensitivity of a color RGB (red, green and blue) chip in a digital camera. Therefore, the image can be split into red, green and blue channels due to the filters that are used within the camera and soil pH value can be analyzed based on red, green, and blue brightness (Merl et al., 2023). The calibration images were captured using the same sensor foils, which was saturated in PBS buffer solutions ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, and NaCl to adjust the ionic strength to 40 mmol L^{-1}) across a range of pH values (4.60, 5.40, 5.86, 6.31, 7.03, 7.35, and 7.61) for 180 min under similar conditions as those for boxes during imaging.

At the end of incubation, i.e. after 60 d, the soil profile in each box was separated into four 2-cm-thick depth (0–2, 2–4, 4–6, and 6–8 cm depth, respectively). Air-dried soil samples were used to determine the pH using a pH-metre combined with a glass electrode (water-to-soil ratio of 2.5:1, v/w) (WTW SenTix 81 pH Electrode, Thermo Scientific Waltham, MA, USA).

Conventionally, ImageJ is generally used to re-calculate the data (Blossfeld, 2013; Ma et al., 2019). The disadvantage is that it is not

available for large samples (Blossfeld, 2013). Here, image processing and analysis were conducted using supervised machine learning in Python (Moen et al., 2019), where fast data analysis can be realized. Each calibration image was used to generate the model for pH prediction. First, 62,500 pixels containing R, G, and B values were sampled from each original calibration image to create the pH RGB dataset with a total size of 437,500. And then, the datasets were split into training and test sub-sets in a 9:1 ratio. For training, we employed a multilayer perceptron (MLP) neural network consisting of two hidden layers, with R, G, and B values as input and pH values as output (Fig. 1). After training, the model was tested on the test sub-set ($\text{RMSE} = 0.009$, $R^2 = 0.991$). This model was subsequently used to predict pH values at the pixel level by inputting R, G, and B values of color on image. The codes can be found online at https://github.com/Taoorwell/soil_ph.git.

2.3. Statistical analyses

Homogeneity of variance for soil pH values was assessed using Levene's test. The least significant difference (LSD) test was used to compare means at $p < 0.05$ of soil pH values of all N fertilizer types at two temperatures. The significant differences between treatments in terms of soil pH depending on temperatures, liming, and depths of image were tested using analyses of variance (ANOVA). All statistical analyses were performed using SPSS (version 21). The correlations between soil pH value measured by the methods of planar optode ($\text{pH}_{\text{optode}}$) and pH-metre combined with a glass electrode ($\text{pH}_{\text{H}_2\text{O}}$) were fitted using linear and piecewise linear (PWL), respectively, and all figures were drawn using Origin 2018.

3. Results

The overall results indicated that the two methods (*in situ* planar optode ($\text{pH}_{\text{optode}}$) and traditional pH-metre ($\text{pH}_{\text{H}_2\text{O}}$)) to determine soil pH value were comparable (Fig. 2). The slope was 1.13 when the $\text{pH}_{\text{H}_2\text{O}}$ value was less than 6.2, closely aligning with the 1:1 line. The $\text{pH}_{\text{optode}}$ was lower than $\text{pH}_{\text{H}_2\text{O}}$ when $\text{pH}_{\text{H}_2\text{O}}$ value exceeded 6.5 (Fig. 2). Therefore, the *in situ* planar optode method was a reliable approach for investigating soil acidification and its results were comparable to that of previous studies employing pH-metre. Fertilization types, temperatures and their interactions affected soil pH (Table 1). The soil pH of

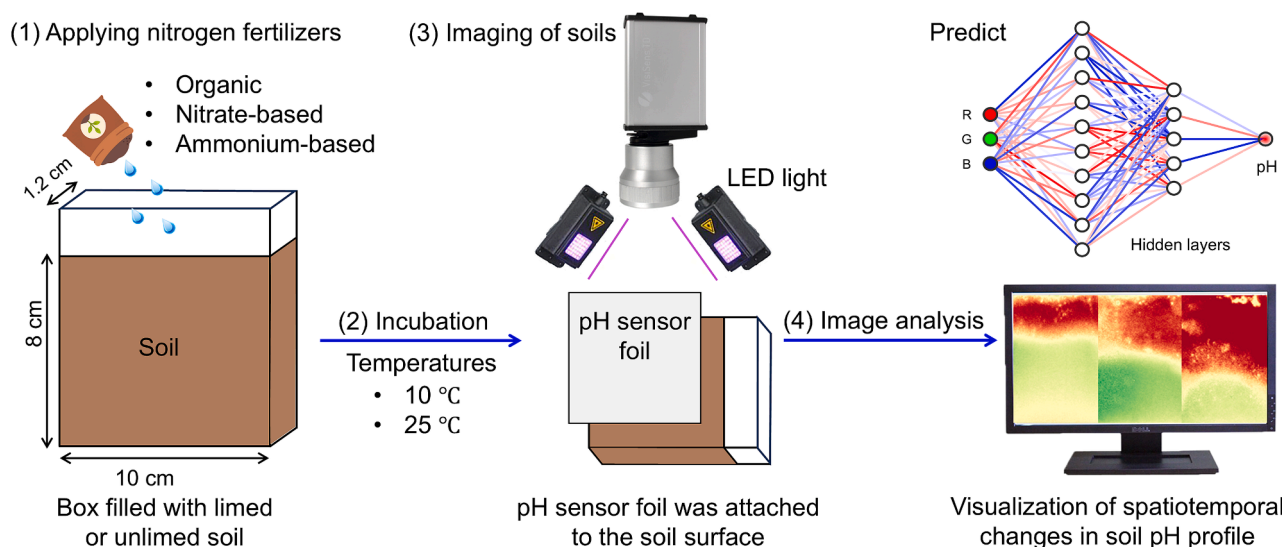


Fig. 1. Experimental design and procedure to visualize spatiotemporal changes of pH values in soil profile as a function of fertilizer type and air temperature during fertilization. (1) Soils in the rhizoboxes were fertilized with different types of fertilizers. (2) Incubated at 10 °C and 25 °C for 5, 12, 20, 40, and 60 d. (3) The rhizoboxes could be opened from one side, enabled imaging of the soil profile, after attaching a pH sensor foil, with a detector connected to a computer. Imaging was also conducted for the pH standards prepared from the PBS buffer solutions i.e. mixing $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ solutions with different ratios. (4) The images were processed to visualize the spatiotemporal distribution of soil pH *in situ*.

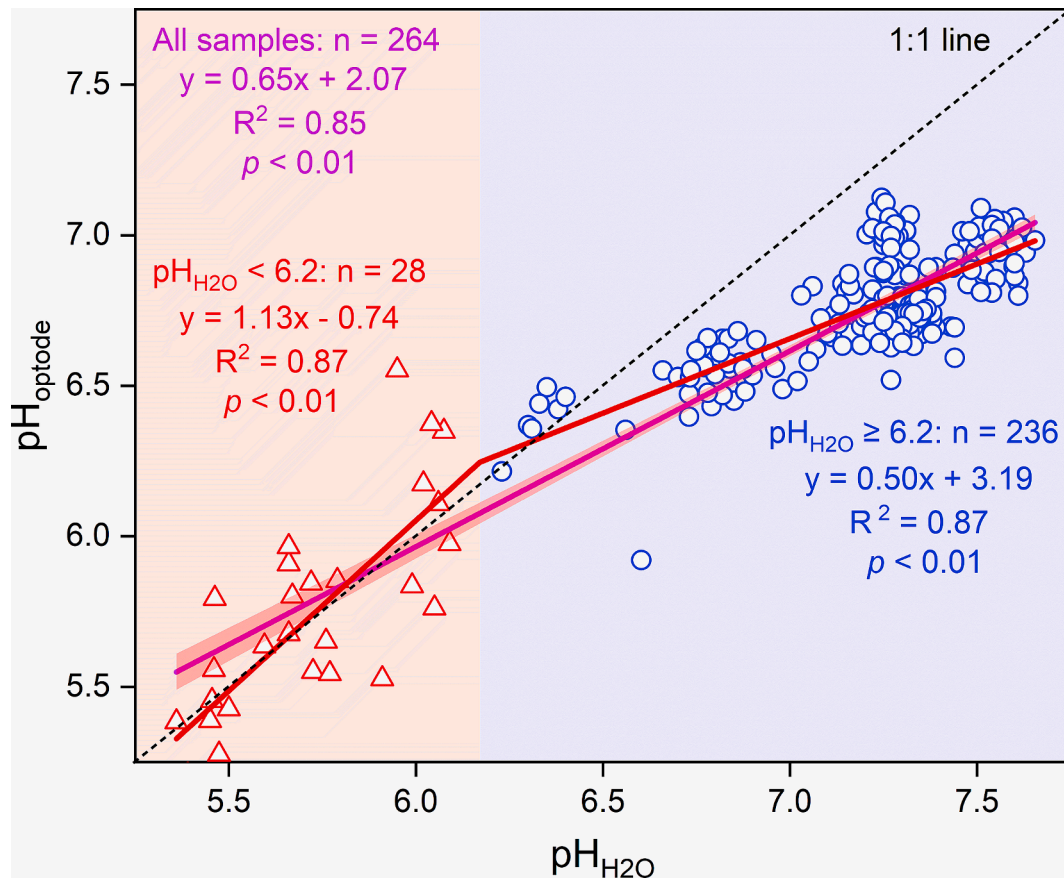


Fig. 2. Correlations between soil pH value measured by the methods of planar optode ($\text{pH}_{\text{optode}}$) and pH-metre combined with a glass electrode ($\text{pH}_{\text{H}_2\text{O}}$). The purple line represents regression lines of all samples data. The red and blue colored bullets and lines represent data points and linear regression line of $\text{pH}_{\text{H}_2\text{O}} < 6.2$ and $\text{pH}_{\text{H}_2\text{O}} \geq 6.2$, respectively.

Table 1

Statistical analysis of the main and interactive effects of N fertilizer type, temperature, and soil depth on soil pH value.

Source	F	Sig.
Fertilization	1674.88	0.000**
Temperature	317.07	0.000**
Soil depth	847.87	0.000**
Fertilization * Temperature	32.91	0.000**
Fertilization * Soil depth	137.73	0.000**
Temperature * Soil depth	9.61	0.000**
Fertilization * Temperature * Soil depth	3.33	0.000**

*Mean significant effects on soil pH at 1% probability level.

ammonium-base N fertilizer treatments was lower than those of nitrate-based N fertilizers and organic fertilizers (Fig. 3). The soil pH value at 10°C was higher than that at 25°C for $(\text{NH}_4)_2\text{SO}_4$, chicken manure, $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$, and $\text{CaCO}_3 + \text{KNO}_3$ fertilizers (Fig. 4). CaCO_3 addition for N_0 , $(\text{NH}_4)_2\text{SO}_4$, and KNO_3 average increased soil pH by 0.65 ± 0.19 units (Fig. 5). The soil acidity depth maximum reached 4.5 ± 0.14 cm within 60 d after the application of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and urea at two temperatures (Figs. 6–8). We only give the spatiotemporal images of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and urea in the text considering the number of ammonium ions in various fertilizer types (Figs. 6–8), and the images of other fertilizers are provided in the supplementary materials.

3.1. Soil pH profile in response to fertilizer types

The soil pH values in the profiles after 60 d of incubation followed the order: $\text{NH}_4\text{H}_2\text{PO}_4 < (\text{NH}_4)_2\text{SO}_4 < \text{NH}_4\text{NO}_3 < \text{urea} < \text{Ca}(\text{NO}_3)_2$,

KNO_3 , $\text{Mg}(\text{NO}_3)_2 < \text{chicken manure}$, Contr-1, especially in top soil depths, 0–2, 2–4, and 4–6 cm (Figs. 3 and 4). The pH of soil profile had no change with time for contr-1 and all nitrate-based fertilizers (Figs. S1–S4). Adding chicken manure increased the soil pH of 0–2 cm after 5 d by 0.29 ± 0.14 – 0.37 ± 0.07 units compared to contr-1 at two temperatures. Thereafter, the soil pH in chicken manure followed a similar trend and value as those for soil pH in nitrate-based fertilizers (Fig. S5).

The ammonium-based N fertilizers decreased the soil pH value by 0.1 ± 0.06 – 2.1 ± 0.08 units compared to contr-1 for all depths and both temperatures (Fig. 3). The pH in the 0–2 cm soil depth, where fertilizers were added, was lower than that in the subsoil (Fig. 3). The acidity diffusion into depths and the degree of acidification increased with incubation time. For example, after adding $(\text{NH}_4)_2\text{SO}_4$ fertilizer, the acidified soil depth extended down to 4.5 ± 0.14 cm over 60 d at 10°C (Fig. 6). The lowest soil pH over 40 d was 1.6 ± 0.02 units lower than that in contr-1 at soil depths of 0–2 cm at 10°C. The soil pH at 2–4-cm-deep soil was the lowest after 60 d, which decreased 1.4 ± 0.16 units compared to contr-1 at 10°C (Figs. S1 and 6). The decreasing rate of soil pH value reached the maximum during 5–40 d and 5–20 d at 10 and 25°C, respectively, was slowing with time, and pH value increased after 40 d at 25°C in 0–4 cm (Fig. 6b and c). The $(\text{NH}_4)_2\text{SO}_4$ addition had no effect on pH at a depth of 5–8 cm over time (Fig. 6a). The application of $\text{NH}_4\text{H}_2\text{PO}_4$ (Fig. S6) had stronger and deeper acidification, and NH_4NO_3 (Fig. 7) had weaker and less deep acidification than that of $(\text{NH}_4)_2\text{SO}_4$ on soil pH profile, respectively.

Urea increased the soil pH by 0.1 ± 0.2 – 0.5 ± 0.06 units in 0–4 cm initially compared to contr-1 during the first 5 d at two temperatures; after that, the trend was the same as that of $(\text{NH}_4)_2\text{SO}_4$ (Figs. S1 and 8). The soil acidity reached 3.9 ± 0.12 cm over 40 d at two temperatures

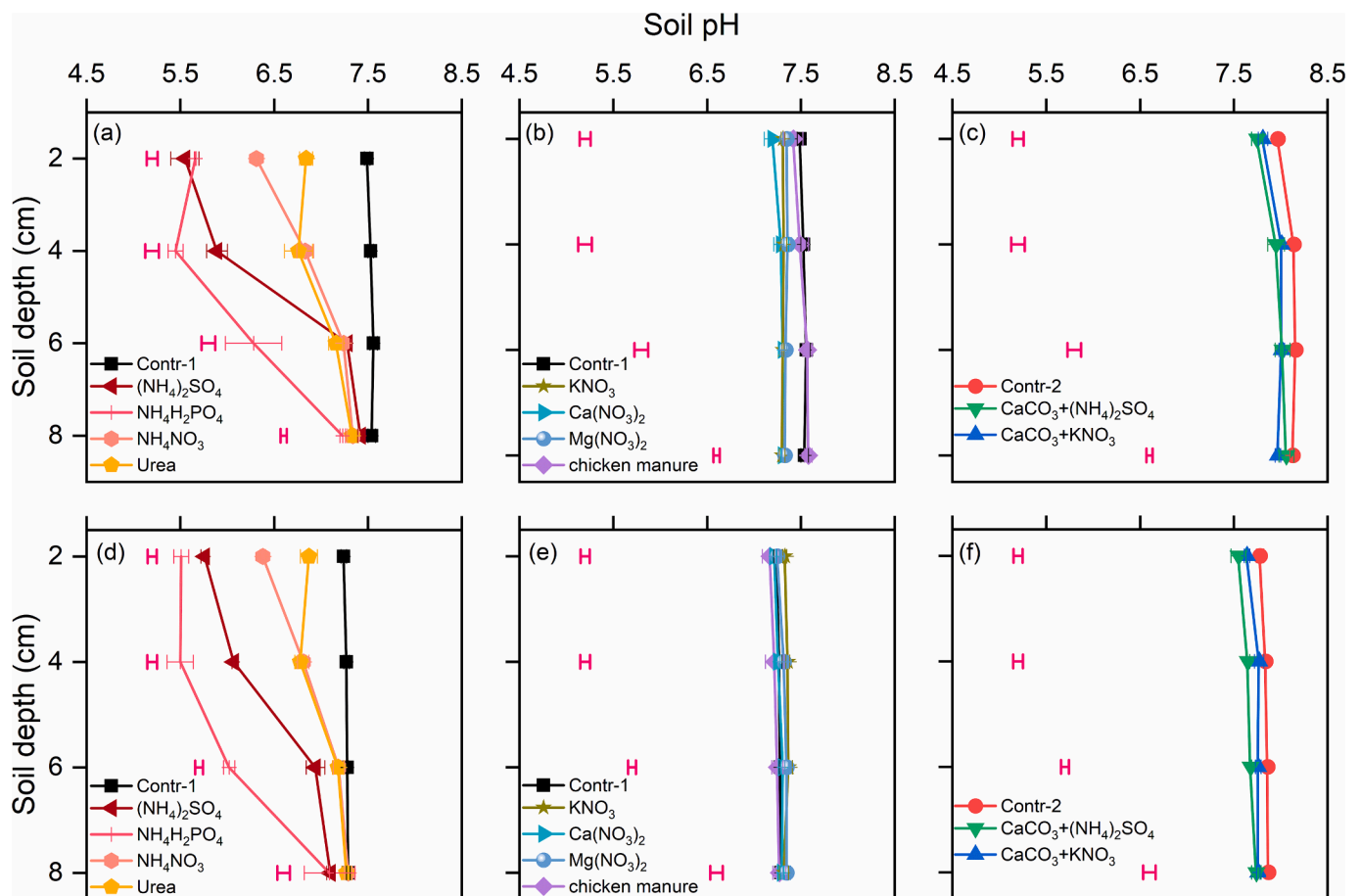


Fig. 3. Effects of N fertilizer types on soil pH profile 60 d after fertilization. Subfigures (a), (b), and (c) show, respectively, the effects of ammonium-based fertilizers, nitrate-based fertilizers, and liming at 10°C. Subfigures (d), (e), and (f) show, respectively, the effects of ammonium-based fertilizers, nitrate-based fertilizers, and liming at 25°C. Horizontal bars on symbols of each treatment and each measuring depth indicate standard deviation (SD). Separate pink bars on the left side of symbols in each subfigure represent LSD at $p < 0.05$.

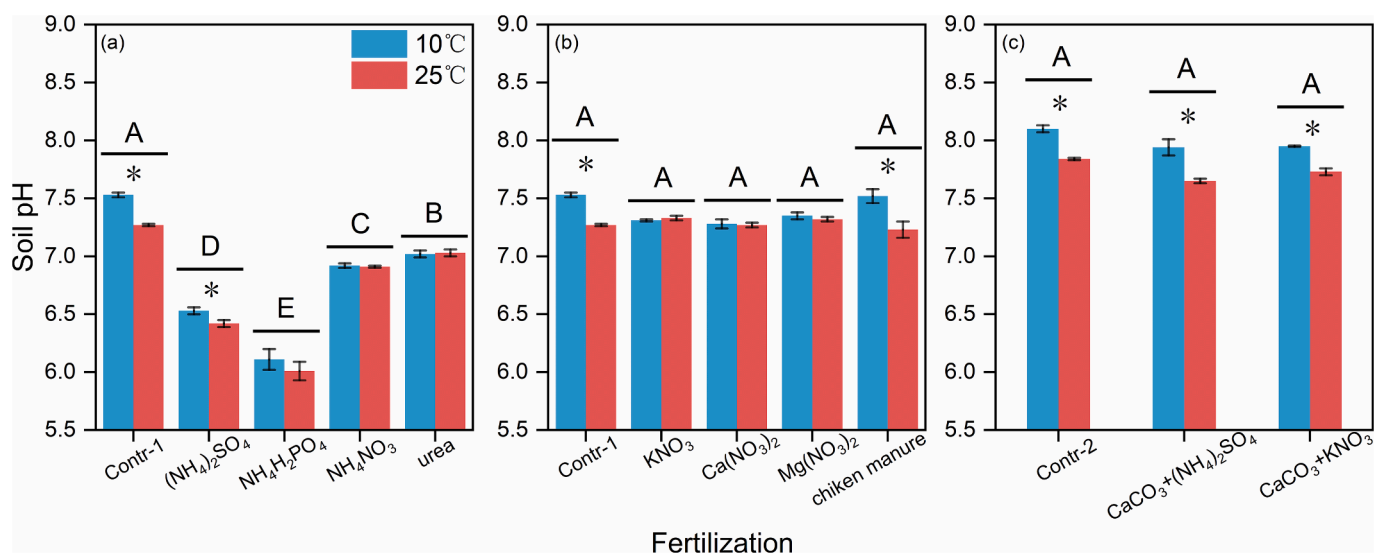


Fig. 4. Effects of temperature and N fertilizer types on averaged soil pH values along the whole profile 60 d after fertilization. Contr-1 is the control that was neither fertilized nor limed. Contr-2 was limed but not fertilized. * indicates significant differences between 10°C and 25°C at a 5 % error probability level. Upper case letters indicate significant differences among fertilizer types at $p < 0.05$.

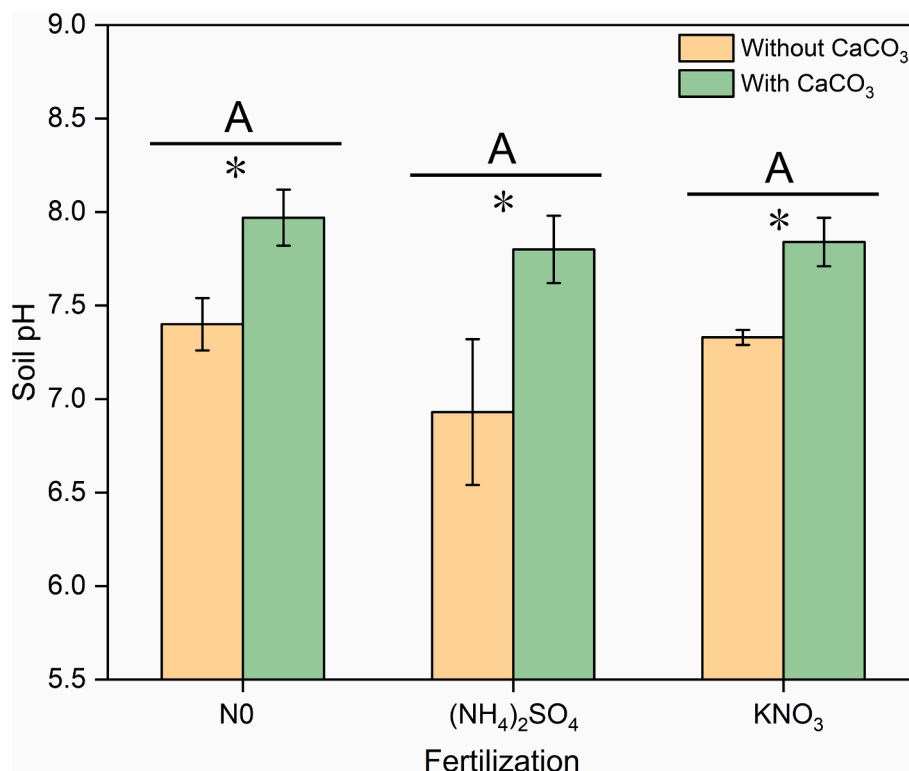


Fig. 5. Effects of CaCO₃ and N fertilizer types on averaged soil pH values along the whole profile 60 d after fertilization. NO is the control without fertilization including contr-1 and contr-2. * indicates significant differences between soils without CaCO₃ and with CaCO₃ addition at a 5 % error probability level. Upper case letters indicate significant differences among fertilizer types at $p < 0.05$.

(Fig. 8a). The pH value reached the lowest in 20 and 40 d at 10 and 25 °C, respectively, i.e. average 1.3 ± 0.15 units smaller than that of contr-1 at soil depths of 0–2 cm (Figs. 8 and S1).

3.2. Soil pH in response to temperature

The soil pH values of contr-1, (NH₄)₂SO₄, chicken manure, contr-2, CaCO₃ + (NH₄)₂SO₄, and CaCO₃ + KNO₃ fertilizers under the 25 °C decreased by 0.1 ± 0.07 – 0.3 ± 0.07 units compared to those at 10 °C (Fig. 4). Higher temperature accelerated the spatiotemporal dynamics of soil acidity. The soil pH decreased following the application of ammonium-based N fertilizers at 25 °C, which was stronger than at 10 °C (Fig. 6). The lowest soil pH at 10 °C occurred in 40 d after (NH₄)₂SO₄ addition at soil depths of 0–2 cm; but at 25 °C, the soil pH at this soil depth was the lowest after 20 d, which decreased faster than that at 10 °C. The soil pH of 2–4 cm at 25 °C decreased to the lowest value after 40 d, which was also faster than that of 10 °C, i.e. 60 d (Fig. 6). At 25 °C, the trend in soil pH value increased first and then decreased as with incubation time due to urea application was similar to that at 10 °C, but the rate and degree of decrease in soil pH profile were higher than those of 10 °C (Fig. 8).

3.3. Effects of liming on the soil pH profile

The soil pH of Contr-2, KNO₃, and (NH₄)₂SO₄ treatments after adding lime increased by 0.57 ± 0.22 , 0.51 ± 0.15 , and 0.87 ± 0.34 units, respectively, compared with those of the soils without liming after 60 d of incubation (Fig. 5). At 10 °C, the pH values of CaCO₃ + (NH₄)₂SO₄ and CaCO₃ + KNO₃ were similar (Fig. 3c). At 25 °C, soil pH at 4 cm soil depth in CaCO₃ + (NH₄)₂SO₄ decreased by 0.12 ± 0.07 units more than that in CaCO₃ + KNO₃ at the end of incubation (Fig. 3f). The soil pH profile of contr-2 was constant over time (Fig. S7). Fertilization of limed soils by (NH₄)₂SO₄ decreased the pH of the 0–4 cm depth by 0.21 ± 0.08

and 0.40 ± 0.07 units over 12 d at 10 °C and 25 °C, respectively (Fig. S8), while the application of KNO₃ had no effect on limed soil pH profiles over time (Fig. S9).

4. Discussion

4.1. Application of planar optode technology for the *in situ* determination and spatiotemporal localization of soil pH profile

Our study found that there was significant correlation between the pH_{optode} and pH_{H2O} methods, especially when pH_{H2O} value was lower than 6.2 (Fig. 2). The *in situ* optode measurements of soil pH were lower than those determined using a pH-metre combined with a glass electrode at pH value above 6.5 at the end of the incubation (Fig. 7b, 8b and c). However, the results of pH-metre method could not indicate the spatial pH change in soil due to the processes of soil crushing, drying, rewetting, shaking (Bornø et al., 2023). It is a bulk measurement method due to the needed soil sample preparation and affects pH value due to the treatment and soil handling (Nielsen et al., 2017). The pH_{H2O} reflects pH in a standardized moisture condition (slurry), considered a laboratory standard. The slurry preparation alters the pH environment, potentially leading to discrepancies when compared to field natural moisture conditions. The pH_{optode} reflects pH *in situ* soil moisture level. Optode relies on the mobility of H⁺ ions, which are affected by soil water. The pH_{optode} value decreases 2 units when the soil water content is lower than 10 % (Merl et al., 2022). Further studies are needed to determine the *in situ* pH value at very dry soil. The pH_{H2O} can serve as a benchmark for calibrating pH_{optode} (Fig. 2). And pH_{optode} method can extend the utility of glass electrode method by offering real-time, *in situ* data in variable field conditions.

Compared to other pH-related imaging techniques (i.e. agar gel and microelectrodes), the change in fluorescence of the indicator dye does not affect the soil and microorganism properties (Schaller and Fischer,

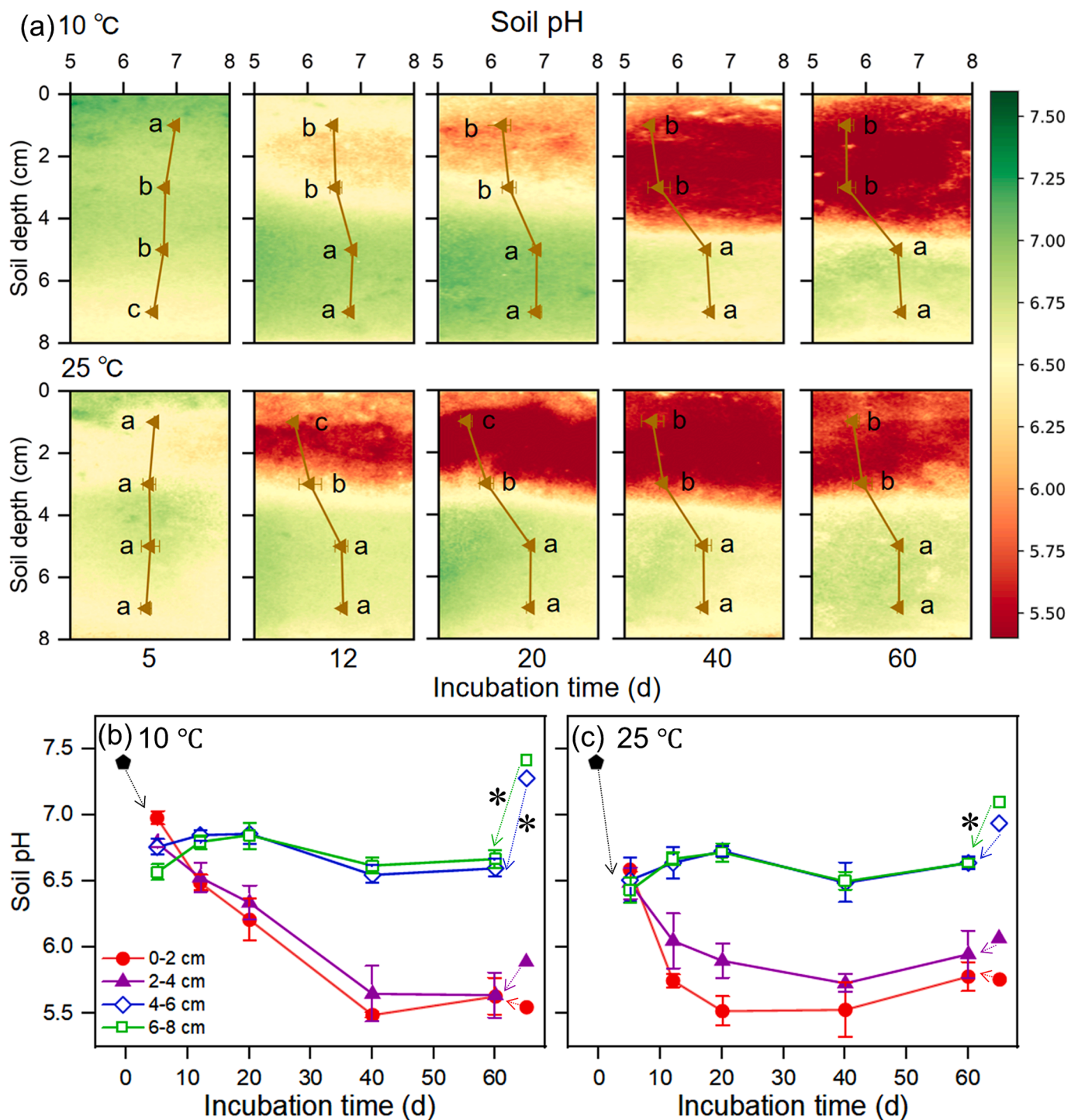


Fig. 6. Spatiotemporal distribution of soil pH and changes after application of $(\text{NH}_4)_2\text{SO}_4$. (a) The above images are from soils incubated at 10°C and those below from soils incubated at 25°C. The size of the image boxes was 4 × 8 cm (width × depth) (134 × 429 pixels), and the width of 4 cm was located in the middle part of the boxes. The top-down triangles represent the average pH value of 0–2, 2–4, 4–6, and 6–8 cm soil depth, respectively. Horizontal bars (smaller or bigger than the symbols) indicate standard deviation (SD) for all fertilizer types. Letters beside the triangles represent significantly different pH values among soil depths ($p < 0.05$). (b) and (c) show the pH changes with time at different soil depths at 10 and 25°C, respectively. The black pentagons indicate the initial soil $\text{pH}_{\text{H}_2\text{O}}$ determined by a pH-metre. The only one reported pH value at the beginning is because of the homogeneous soil profiles before fertilizer addition. The last four symbols with arrows indicate the $\text{pH}_{\text{H}_2\text{O}}$ values determined at the end of the incubation in 2-cm-thick separated depths of each soil profile using a pH-metre. * indicates significant differences between *in situ* optode measurements of soil pH and the values determined by a pH-metre at a 5 % error probability level.

1981; Li et al., 2007; Rudolph-Mohr et al., 2017). It also possesses high-resolution (2–200 μm in space), allowing the drawing of real-time and quantitative maps of soil pH (Blossfeld, 2013; Merl et al., 2024). Therefore, the planar optode technology is a more credible approach to allow the non-invasive acquisition of the spatiotemporal localization of

pH in soil profiles. It provides a two-dimensional mapping of pH distribution, making them particularly suitable for studying heterogeneous soil environments.

Soil acidification hotspots occurred after the addition of ammonium-based N fertilizers, with the magnitude of H^+ production influenced by

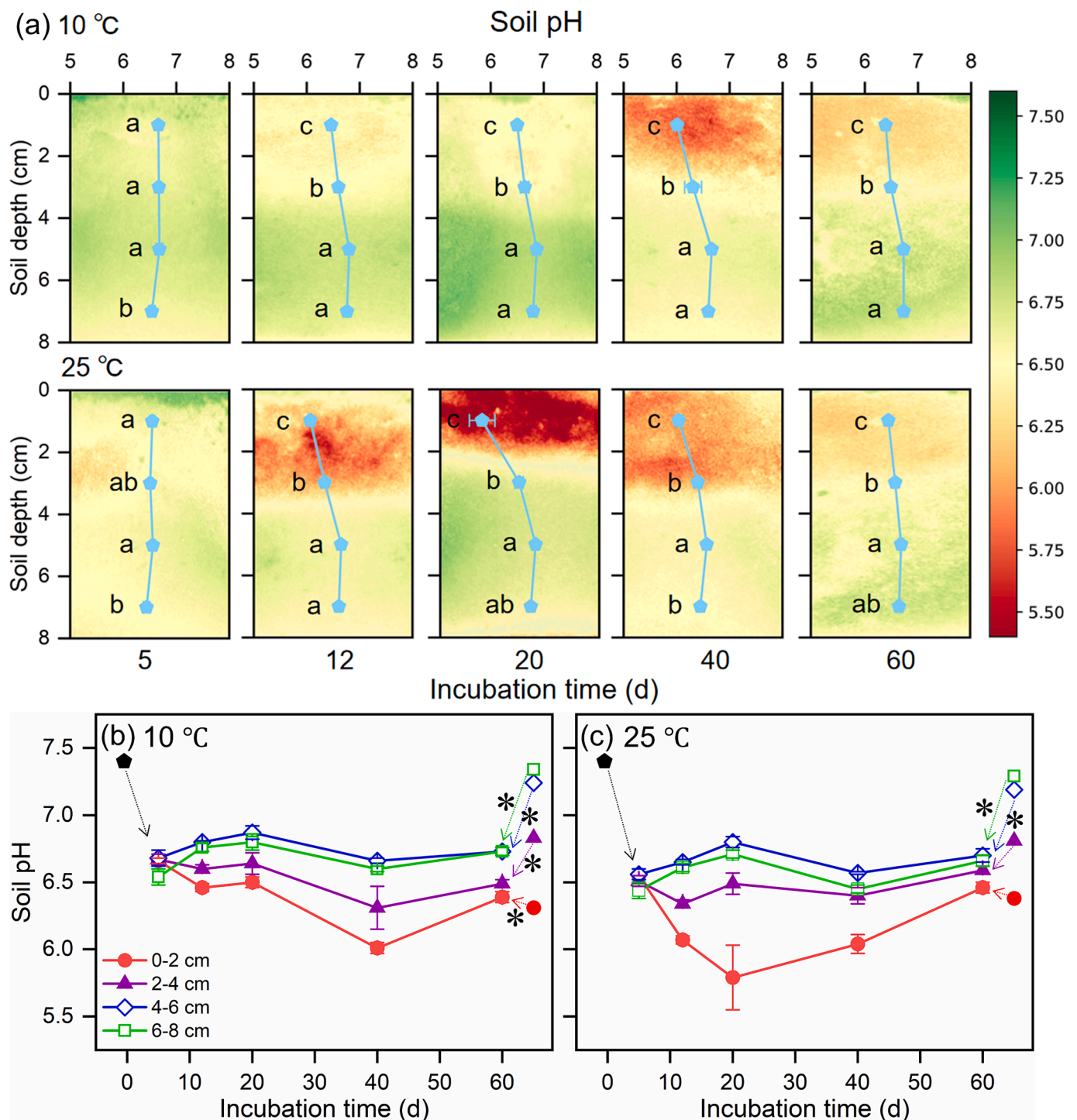


Fig. 7. Spatiotemporal distribution of soil pH and changes after application of NH_4NO_3 . The explanations about sub-figures are as mentioned in Fig. 6.

ammonium contents and nitrification rate (Figs. 6–8 and S6) (Tian and Niu, 2015; Hao et al., 2020; Wang et al., 2023). The nitrification rate was higher after application of ammonium sulfate than that of ammonium nitrate and urea fertilizers by using the same soil samples and treatments in Tao et al., (2024). This supports our first hypothesis that ammonium-based N fertilizers induced the strongest soil acidification in croplands and $(\text{NH}_4)_2\text{SO}_4$ is a stronger acidifier than NH_4NO_3 (Fig. 3a, d, 4a and 5) (Chien et al., 2008; Liu et al., 2021a; Han et al., 2022; Uwiragiye et al., 2023). The soil pH increased shortly after urea application because the OH^- and NH_4^+ ions produced by its hydrolysis, followed by a decrease as nitrification progressed (Tisdale et al., 1985;

Sigurdarson et al., 2018; Liu et al., 2021a; Rex et al., 2021). Although urea and NH_4NO_3 produced equivalent numbers of H^+ , the acidifying effect of urea was mitigated by OH^- ions released during its hydrolysis (Fig. 3a, d and 4a). Therefore, choosing the right N fertilizer type is important to control soil acidification, especially at region where the soil is already acidic.

The images of soil profile pH directly visualize its spatiotemporal distribution. Topsoil was the first to become most acidic when N fertilizers were applied on the soil surface (Figs. 6–8 and S6), but the acidity was infiltrated deeper by diffusion. Nitrification in the top soil increases the NO_3^- -N concentration; and there is a negative exponential correlation

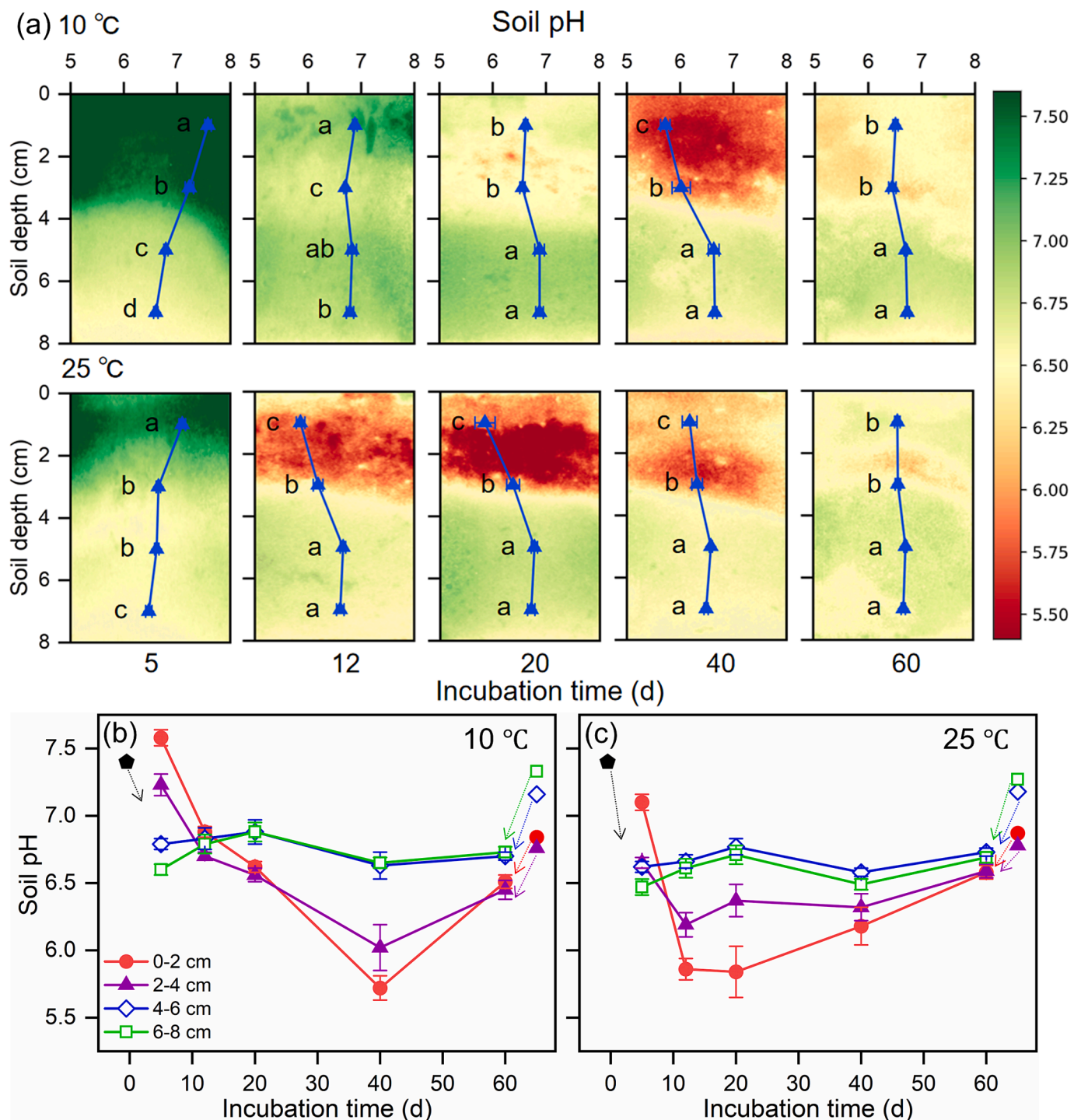


Fig. 8. Spatiotemporal distribution of soil pH and changes after application of urea. The explanations about sub-figures are as mentioned in Fig. 6. Note that the differences between the estimated pH values via in situ optode and the measured values with a pH-metre at the end of the experiment were significantly different at 5% error probability level in all depths after urea application. Therefore, for a better visualization and in contrast to Figs. 5 and 6, no * is added in subfigures (b) and (c).

between soil pH and $\text{NO}_3\text{-N}$ until up to 21.9 mg kg^{-1} (Souza et al., 2023). This acidity transport can be supported by the observed higher concentrations of basic cations such as Ca^{2+} and Mg^{2+} and nitrate ions leached to deeper depths in soils treated by N fertilizers than those of non-fertilized soils (Yan et al., 2018; Li et al., 2020; Zhu et al., 2023b). Obviously, using simple destructive sampling and artificially segmenting soil layers could not observe the effects of N fertilizers on the spatial variation of soil pH. The decreasing rate of soil pH at 0–2 cm was the

greatest within 12 d, and thereafter became slower till 40 d (Fig. 6). Because the high amount of ammonia or ammonium near the N fertilizer at first 5 d may have suppressed the nitrification activity due to ammonia toxicity. As the ammonium were consumed and decreased pH value, the stronger nitrification process between 5–12 d and nitrification activity is greatest by affecting AOB *amoA* gene abundance and modulated *amoA* gene transcription (Merl et al., 2024; Tao et al., 2024). The presence of CaCO_3 , i.e. the strongest soil buffer substance (Raza et al.,

2021; Li et al., 2023b), is the reason of increasing soil pH values from 40 to 60 d (Fig. 6). Despite the acidity reached 4.5 ± 0.14 cm depth due to large amount of H^+ generation (Merl et al., 2024), especially following the application of $(NH_4)_2SO_4$ and NH_4NO_3 , with an initial sharp decrease in soil pH, neutralization of part of the generated protons by soil native $CaCO_3$ led to a slow pH increase towards the end of the incubation (Figs. 6–8). Although, theoretically the whole H^+ released from the nitrification of ammonium-based N fertilizers can be neutralized by $CaCO_3$ (Table S1), soil pH value still decreased within 40 d (Figs. 6–8). Therefore, it's necessary to monitor the pH change of N fertilizers on *in situ* soil pH over time.

Soil acidification due to fertilization depends on temperature. The faster temporal and spatial processes in soil pH profiles at 25°C (Figs. 4 and 6–8) supports our second hypothesis that fast nitrification rate induced by high temperatures after fertilization led to stronger soil acidification. Therefore, temperature should be considered during fertilization management as fertilizing on relatively cooler days, when the temperature is relatively low, will reduce subsequent acidification.

4.2. Lower rates of soil acidification by nitrate-based fertilizers, manure, and liming compared with ammonium-based fertilizers

Our results indicated that fertilization by $Ca(NO_3)_2$, KNO_3 , and $Mg(NO_3)_2$ produces no direct H^+ , but also brings extra Ca^{2+} , Mg^{2+} , and K^+ to soil, which effectively buffered acidity and even increase bulk soil pH (Figs. S2, S7 and S8). The low rate of soil acidification by organic fertilizers (Fig. 3b, e and 4b) is explained by the mineralization processes, where (1) decarboxylation of organic anions offsets H^+ (Dippold et al., 2014; Hussain et al., 2023), (2) release of base cations such as Ca^{2+} neutralizes acidity (Liu et al., 2021b), and (3) the slow N release during the decomposition of organic fertilizers, together with the increased N assimilation by microorganisms due to C addition, reduces unassimilated N available for nitrification and the subsequent H^+ production compared with only N addition (Ning et al., 2022). Thus, partial substitution of mineral N fertilizer (ammonium-based N fertilizer) with manures could mitigate soil acidification. The type and amount of N fertilizers should be selected rationally, according to crop needs and nutrient availability.

Temperature intensifies the mineralization of organic compounds (Jia et al., 2020). Therefore, the soil pH at the end of the incubation decreased more after organic fertilizer application at 25°C compared to 10°C (Fig. 4b). Nevertheless, the mineralization of organic N is a slow and prolonged process (Cassidy-Duffey et al., 2020; Uddin et al., 2021). The long-term bare fallow experiment conducted by the French National Research Institute for Agriculture, Food and Environment since 1928 revealed that the soil pH decreased by about 1 unit due to decomposition of organic matter during the first 10 to 15 years (Van Oort et al., 2022). Therefore, the ultimate effect of organic fertilizers on soil acidification should be monitored over relatively longer application times (Jia et al., 2022; Liu et al., 2023).

Protons could move deeper in the soil by preferential flow through the large pores in soil. The protons generated at the surface reached the depth of more than 4 cm in only 10–40 d depending on fertilizer types (Figs. 6–8 and S6). Such sub-soil acidification in the field poses a serious threat to crop production because it is difficult to modify sub-soil pH and there is no simple practical approach to improve it (Zamanian and Kuzyakov, 2022). The addition of lime, which is commonly used to correct soil pH (Zhang et al., 2023; Raza et al., 2024a), can generally neutralize protons in the topsoil (Fig. S8). Targeting the sub-soil may necessitate the application of considerably larger lime amounts. Hence, if the $CaCO_3$ content in the topsoil is depleted, sub-soil acidification will have irreversible drawbacks on soil health.

Soil pH is controlled via cation exchange and the base saturation after complete decalcification (Raza et al., 2020; Zamanian et al., 2024). However, the exchangeable cations alone cannot rapidly neutralize H^+ , and in the absence of $CaCO_3$ the soil pH keeps decreasing and goes below

6 (Zamanian and Kuzyakov, 2022; Raza et al., 2024b). Additionally, decalcification of cropland areas provides a net source of CO_2 at global scales (Zamanian et al., 2018; Song et al., 2022; Tao et al., 2022; Tao et al., 2024). Therefore, the $CaCO_3$ content of the topsoil should be monitored and considered as a measure of vulnerability of the sub-soil to acidification.

The spatiotemporal dynamics of soil acidification under field conditions should be more complex (Ma et al., 2019; Tao et al., 2022; Zhu et al., 2024). Therefore, further studies are needed to employ the planar optode technology in the field. The 'optodes pH mapping system' is a portable meter and easy to bring to the field. This *in situ* soil pH imaging can be achieved by installing stationary root window in the field and can combine planar optode technology with zymography and diffusive gradients in thin films (DGT) techniques (Vetterlein et al., 2020; Bilyera et al., 2022; Bornø et al., 2023). Soil organic matter content varies across different locations in field conditions, which can release humic substances, thereafter may absorb or interfere with the optode's fluorescent signal (Bornø et al., 2023). The buffering effect of organic matter affect the response of optode to H^+ ions. Soils with high organic matter content may require specific calibration curves for accurate pH measurement. Future research could focus on developing specific calibration models or algorithms for optode sensors that account for the interference from organic matter.

5. Conclusions

Our study found that there was significant correlation between the pH_{optode} and pH_{H_2O} methods. The planar optode enabled *in situ* mapping of the spatial and temporal changes in soil pH profile following the addition of different types of fertilizers. Soil pH decreased much more and faster with ammonium-based N fertilizers than with nitrate-based and organic fertilizers during two months after application. The $NH_4H_2PO_4$ was the strongest acidifier, followed by $(NH_4)_2SO_4$, and NH_4NO_3 . Higher temperature resulted in faster temporal and broader spatial acidification in the soil profile. The generated protons were transferred into depths when the soil $CaCO_3$ content was low, liming mitigates the acidification caused by N fertilizers. Therefore, the type and amount of N fertilizers should be selected rationally not only according to crop needs and nutrient availability, but also in relation to soil carbonate content or liming potential and ambient environmental temperature. The planar optode is a powerful non-invasive imaging technique that enables *in situ* visualization of the spatiotemporal changes in the soil pH profile after fertilization in rhizobox studies. More studies are needed to apply this method in the field due to the diversity and dynamic changes of precipitation, temperature, irrigation, tillage, etc.

CRedit authorship contribution statement

Jingjing Tao: Writing – original draft, Visualization, Software, Methodology, Funding acquisition, Formal analysis, Data curation. **Lichao Fan:** Writing – review & editing, Software, Data curation. **Tao Jiang:** Software, Data curation. **Xiaona Song:** Software, Methodology. **Mengzhen Zhao:** Methodology. **Jianbin Zhou:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Yakov Kuzyakov:** Writing – review & editing, Funding acquisition, Conceptualization. **Kazem Zamanian:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2025.117243>.

Data availability

Data will be made available on request.

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