Agriculture, Ecosystems and Environment 393 (2025) 109863

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Changes rather than absolute contents of soil nitrogen, phosphorus, potassium, and calcium are responsible for soil-profile acidification in apple production systems

Haotian Shi [a,1], Shilong Sun [a,1], Zhanjun Liu [a,b,*], Yuanjun Zhu [c], Chao Ai [d], Xinpeng Xu [d], Zhaohui Wang [a]

[a] College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi 712100, China
[b] State Key Laboratory for Crop Stress Resistance and High-Efficiency Production, Northwest A&F University, Yangling, Shaanxi 712100, China
[c] College of Soil and Water Conservation Science and Engineering, Northwest A&F University, Yangling 712100, China
[d] Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China

ARTICLE INFO

Keywords:
Soil acidification
Land use change
Deep soil profiles
Overfertilization

ABSTRACT

Overfertilization in farmland-to-orchard conversion is causing severe deep soil acidification on the Loess Plateau, China. Although fertilizer nitrogen is the primary factor causing acidification, little is known about the contributions of other soil nutrients. Here, we investigated the vertical distributions of pH and available nutrients in deep soil profiles in croplands and rainfed and flood-irrigated apple orchards of different ages. Depth-averaged pH decreased by 0.25 units in 25-yr rainfed orchards and by 0.29 units in 30-yr irrigated orchards, although pH increased linearly with depth in all systems. However, compared with pH absolute values, differences in the relations between changes in soil pH (ΔpH, difference from "control" cropland) and depth suggested that changes in cropland soil pH might mask the responses of soil pH in orchards. The relations between soil pH and available nutrients differed substantially from those between ΔpH and Δavailable nutrients. Nonsignificant relations between ΔpH and ΔNO_3^--N in 8-yr rainfed orchards and 10-yr irrigated orchards indicated that the changes in rather than the absolute values of soil NO_3^--N accounted for deep soil acidification. Partial least squares path models indicated that deep soil acidification was primarily associated with ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca, compared with absolute values. The contributions of Δavailable nutrients to ΔpH were typically dependent on irrigation, land-use types, and soil depths. Our study demonstrates that changes in available nutrients are better indicators than their absolute values of soil acidification in Chinese apple production systems.

1. Introduction

Soil acidification ranks fourth among global soil degradation processes and increasingly threatens agricultural sustainability (FAO and ITPS, 2015). The current acidification induced by anthropogenic factors, especially nitrogen (N) fertilization, is attracting the attention of pedologists. For example, Guo et al. (2010) reported that average topsoil pH declined by 0.50 units in major Chinese croplands from the 1980s to the 2000s, and Zamanian et al. (2024) found severe ongoing acidification in European croplands resulting from N fertilization. A global analysis covering 1900–2014 found that N deposition decreased average topsoil pH by 0.14 units in grassland and by 0.50 units in forest (Tian and Niu, 2015). To date, topsoil acidification (i.e., 0–20 cm) and its potential mechanisms in cereals (i.e., wheat, maize, and rice) and natural grass–forest systems with low N input have been extensively explored (Zeng et al., 2017; Wu et al., 2022; Zamanian et al., 2024). However, little information is available for apple production systems that are characterized by relatively high N input and deep root systems (Wang et al., 2015b; Liu et al., 2019), although severe topsoil acidification (i.e., 0–30 cm) is sporadically reported (Ge et al., 2018; Zhao et al., 2023). Thus, an in-depth understanding of soil acidification is urgently needed for devising site-specific mitigation strategies for overfertilized orchards in apple-producing countries such as China, Brazil, Egypt, and India.

* Correspondence to: College of Natural Resources and Environment, Northwest A&F University, Xinong Road, #3, Yangling, Shaanxi 712100, China.
E-mail address: zjliu@nwsuaf.edu.cn (Z. Liu).
[1] The two authors contributed equally to this work.

https://doi.org/10.1016/j.agee.2025.109863

Available online 17 July 2025

The consensus is that soil N is responsible for soil acidification (Guo et al., 2010; Zamanian et al., 2024). However, significant declines in pH and equivalent low levels of nitrate-N (NO_3^--N, <5 mg kg^{-1}) in soils deeper than 6 m indicate that soil N cannot fully explain soil acidification (Chen et al., 2022; Ren et al., 2023). Several long-term experiments in cereal production systems demonstrate that soil pH decreases significantly in NK- and NP-treated soils compared with that in soils with N application alone (Xiao et al., 2020; Zhao et al., 2023). Similar results are also recorded in vegetable production systems (Lv et al., 2020). Unfortunately, soil available phosphorus (AP) and potassium (AK) are always ignored despite their significant and widely observed effects on soil acidification (Han et al., 2020). In addition, $CaCO_3$ is the most important component affecting soil acid buffering capacity in calcareous soil (Zamanian et al., 2024), and $CaCO_3$ dissolution and the leaching and reprecipitation of Ca^{2+} strongly regulate soil acidity (Raza et al., 2020). The VSD+ model was specifically developed using NO_3^--N, HPO_4^{2-}, K^+, and Ca^{2+} to simulate soil acidification but with relatively little data (Zeng et al., 2017). Therefore, to comprehensively explore soil acidification, soil NO_3^--N, AP, AK, and exchangeable Ca (Ex-Ca) must be considered.

Overfertilization with N–P_2O_5–K_2O in Chinese apple orchards substantially changes soil nutrients in deep profiles, although the effects are greater in topsoils than in subsoils (Chen et al., 2022; Rezapour et al., 2024; Zhao et al., 2024). Compared with cereal crops, apple trees have deep root systems, reaching to 18 m in depth (Wang et al., 2015b), and thus, converting cropland to apple orchards inevitably depletes soil nutrients in deep soil layers (Droue et al., 2015), ultimately affecting vertical distribution patterns of soil chemical properties. Therefore, to examine soil acidification in apple production systems, the characteristics of soil pH in deep profiles need to be determined. Soil pH generally increases with soil depth in 21-m soil profiles irrespective of land-use types across the Chinese Loess Plateau (Wang et al., 2022), whereas soil nutrients, such as NO_3^--N and K^+, generally decrease with depth (Zhao et al., 2024). Consequently, soil pH and nutrients are significantly negatively related with increasing depth in most cases, but causal factors have not been identified. For example, Ren et al. (2023) reported a significant exponential negative relationship between soil pH and NO_3^--N in 0–10-m deep profiles of rainfed apple orchards on the Loess Plateau; however, the relation differed in soils deeper than 6 m, with significant declines in pH but also low levels of NO_3^--N (<5 mg kg^{-1}). Thus, the regression analysis based on absolute values of soil properties did not correctly evaluate the contributions of driving factors to soil acidification induced by land-use change in deep soil profiles. To correctly identify the factors driving soil acidification, regression analysis needs to be based on the changes in rather than the absolute values of soil NO_3^--N and pH.

The Loess Plateau in China accounts for 25.6 % of the global apple cultivation area (FAOSTAT, 2022; NBSC, 2022). However, apple orchards on the plateau are overfertilized, with exceptionally high inputs of chemical N–P_2O_5–K_2O fertilizers of 1200–675–900 kg ha^{-1} yr^{-1} (Liu et al., 2019). Moreover, flood irrigation of > 800 m^3 ha^{-1} yr^{-1} is widely practiced in irrigated apple orchards (Zhang et al., 2021), which subsequently increases the leaching of NO_3^--N and base cations to deeper soil layers, complicating fertilization-induced effects on soil acidity in deep layers (Zhu et al., 2022). Unfortunately, whether soil acidification occurs in irrigated apple orchards and its potential driving mechanisms have not been investigated to date. The leaching of NO_3^--N does not exceed 6 m in rainfed and 11 m in irrigated apple orchards (Liu et al., 2019; Zhu et al., 2022). With its thick loess deposits, the Loess Plateau provides an ideal platform to investigate the vertical characteristics of pH in deep soils in rainfed and irrigated apple production systems (Zhu et al., 2018). Here, we used deep soil profiles to examine how the conversion of cropland to orchards of different stand ages affected soil acidification in flood-irrigated and rainfed apple-producing regions on the Loess Plateau. We analyzed the vertical distributions of pH and available nutrients by comparing absolute values with the changes in these values (Δ). Our objectives were to (i) explore the characteristics of pH vertical distribution in deep soil profiles, (ii) identify the relations between soil pH and NO_3^--N, AP, AK, and Ex-Ca and those between changes in pH (ΔpH) and changes in NO_3^--N (ΔNO_3^--N), AP (ΔAP), AK (ΔAK), and Ex-Ca (ΔEx-Ca), and (iii) quantify the contributions of soil NO_3^--N, AP, AK, and Ex-Ca to soil acidification in rainfed and irrigated apple production systems. We hypothesized that (1) irrigation would increase the depth and the extent of soil acidification in deep layers of apple orchards, (2) soil NO_3^--N, AP, AK, and Ex-Ca would jointly regulate soil acidity, and (3) the changes in rather than the absolute values of soil NO_3^--N, AP, AK, and Ex-Ca would better explain the soil acidification.

2. Materials and methods

2.1. Study sites

The study was conducted in the counties of Liquan (34°20′50″N, 108°28′40″E; ~565 m a.s.l.) and Luochaun (35°47′47″N, 109°35′37″E; ~1100 m a.s.l.), which are typical irrigated and rainfed apple-producing regions, respectfully, on the Loess Plateau, China (Fig. 1). The study area has a temperate continental monsoon climate. Mean annual precipitation (MAP) and temperature (MAT) are 555 mm and 13.9°C, respectfully, in Liquan County and 586 mm and 9.2°C, respectively, in Luochuan County. Approximately 65 % of MAP occurs between June and September (1982–2022) (Fig. 2). The soil in irrigated and rainfed apple orchards is silty loam of loess deposits, classified as Calcaric Cambisol (IUSS Working Group WRB, 2014). The groundwater level is ~15–30 m below the soil surface in Liquan County, whereas it is usually > 100 m below the soil surface in Luochuan County (Zhu et al., 2018).

2.2. Experimental design and soil sampling

Profiles 6 m deep and 13 m deep are potentially robust for evaluating the dynamics of soil NO_3^--N in rainfed and irrigated apple-producing regions, respectively (Liu et al., 2019; Zhu et al., 2022), and the consensus is that soil acidification primarily results from NO_3^--N (Guo et al., 2010; Zeng et al., 2017). Therefore to investigate the vertical characteristics of soil pH and NO_3^--N in response to cropland-to-orchard conversion, fifteen 6-m soil profiles with 20-cm intervals were sampled from each permanent cropland (as the control) and 8-yr, 17-yr, and 25-yr apple orchards from the typical rainfed apple-producing region of Luochuan County during the harvest period in October 2017, and twenty 13-m profiles with 20-cm intervals were sampled from five permanent croplands and five representative apple orchards of stand ages 10, 20, and 30 years from the typical irrigated apple-producing region of Liquan County during the harvest period in October 2022. Sample locations are shown in Fig. 1. All of the orchards were formerly cropland before being planted with apple trees. The croplands were cropped with winter wheat and summer maize rotation, and in the orchards, apple tree spacing was 4 m × 3 m (825 trees ha^{-1}). Overall, 3100 soil samples (rainfed region: 60 profiles × 30 20-cm intervals; irrigated region: 20 profiles × 65 20-cm intervals) were collected between rows using a 20-cm soil auger (5-cm diameter).

All sampled orchards were planted with the apple cultivar Fuji (*Malus pumila* Mill.), which covered approximately 70 % of the orchard area on the Loess Plateau (Zhao et al., 2023). The fertilization schedules were 950–600–600, 1150–900–900, and 1100–900–900 kg ha^{-1} yr^{-1} of N-P_2O_5–K_2O for the 10-, 20- and 30-year-old apple orchards in the irrigated region, and 450–375–360, 1200–900–900, and 1200–900–900 kg ha^{-1} yr^{-1} for the 8-, 17- and 25-year-old apple orchards in the rainfed region, respectively. Fertilization practices and histories were consistent for apple orchards in both the irrigated and rainfed regions (Wang et al., 2013; Zhang et al., 2023). The compound fertilizers (15–15–15 or 19–19–19), K_2SO_4, and urea were applied three times (1.0 m from the trunk) per year along the tree rows using machinery or by manually digging a fertilization band (~20 cm depth,

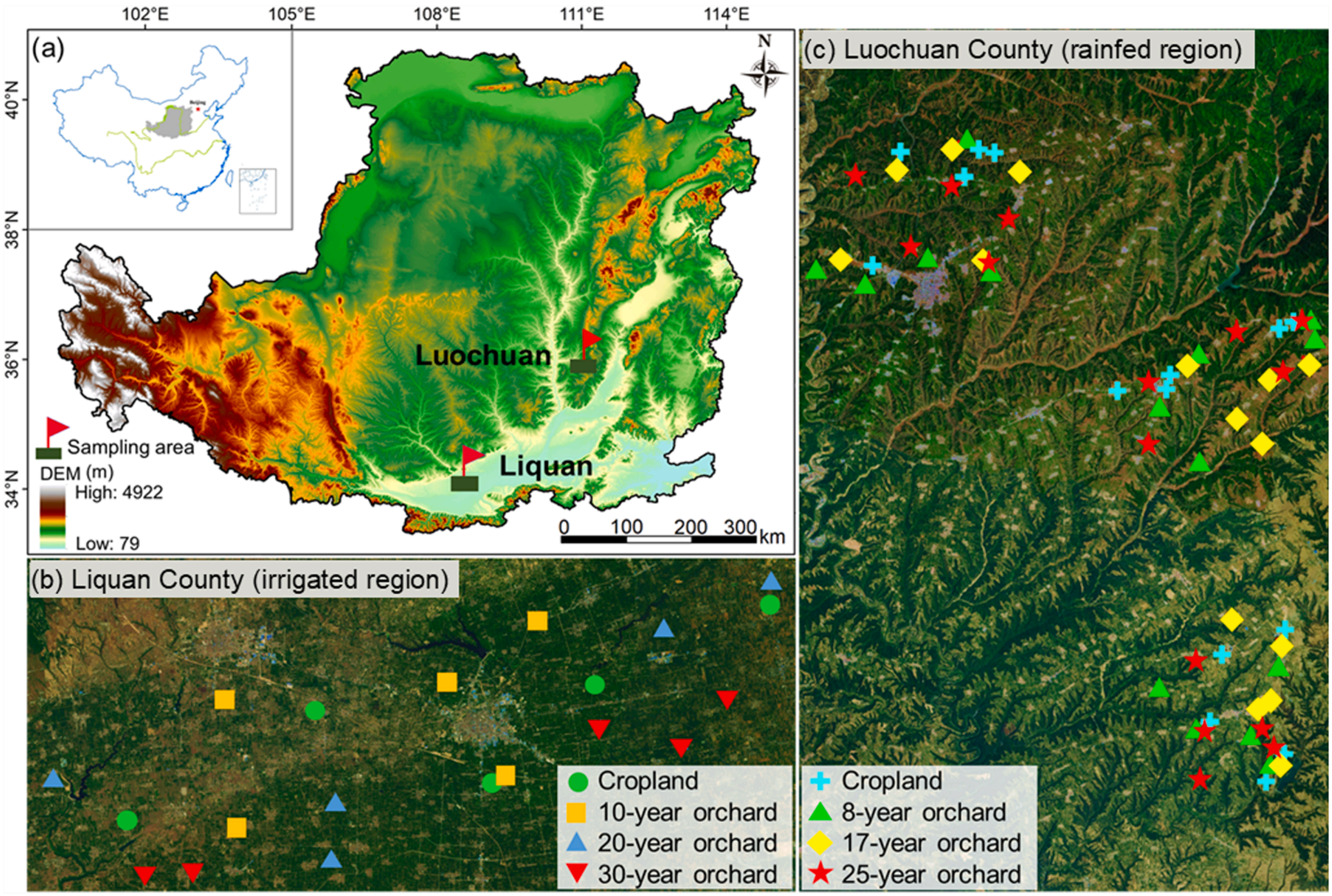

Fig. 1. Locations of the Loess Plateau in China (a) and the sampling sites in irrigated (b) and rainfed region (c).

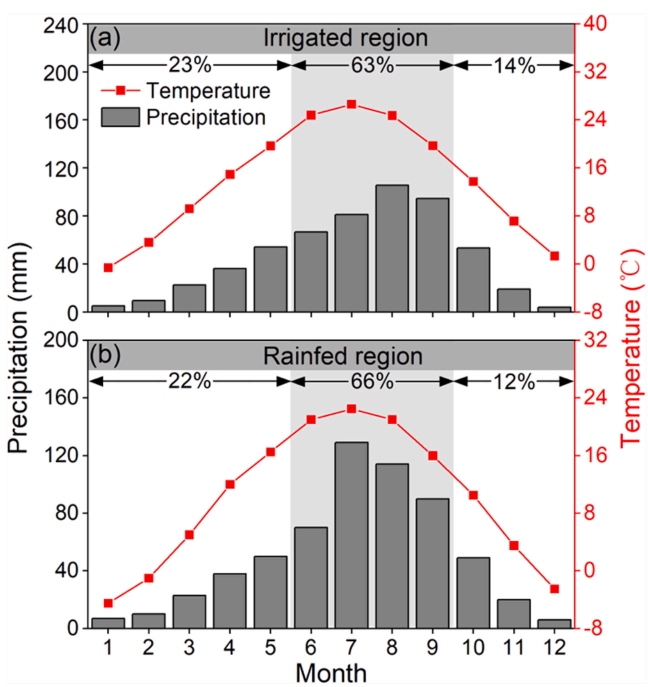

Fig. 2. Monthly-averaged precipitation and temperature in an irrigated region of Liquan County (a) and in a rainfed region of Luochuan County (b) from 1982 to 2022.

~25 cm width) around each apple tree, at a ratio of 4:3:3 corresponding to the post-harvest, bud break, and fruit enlargement periods. For the irrigated and rainfed croplands, N–P_2O_5–K_2O fertilizers at 190–120–0 kg ha^{-1} were applied as basal fertilizers and were evenly broadcast onto the soil surface and immediately incorporated into plowed soil (0–20-cm depth) by machinery in late September (Zhao et al., 2016). In the irrigated apple-planting region of Liquan County, the 10-, 20- and 30-year-old orchard irrigation volumes were 1500, 1800 and 1800 m^3 ha^{-1}, at a ratio of 1:1:1 corresponding to the post-harvest, bud break, and fruit enlargement periods, respectively.

2.3. Soil analyses

Soil pH was measured using air-dried samples with a soil:water ratio of 1:2.5, as determined by a glass electrode (FiveEasy Plus, Mettler Toledo, Zurich, Switzerland). The soil water content (SWC) was determined as the proportion of mass loss in a sample segment during oven-drying to a constant weight at 105°C. Soil NO_3^--N was extracted using 1 mol L^{-1} KCl and then determined using a continuous flow analyzer (AA3, SEAL, Norderstedt, Germany). Available phosphorus (AP) was extracted using 0.5 mol L^{-1} $NaHCO_3$ (pH 8.5) and then analyzed by a spectrophotometer (Lambda 1050 +, Perkin Elmer, Waltham, MA, USA). Available potassium (AK) and exchangeable calcium (Ex-Ca) were extracted with 1.0 mol L^{-1} CH_3COONH_4 and then measured by atomic emission spectrophotometry and atomic absorption spectrophotometry (PinAAcle 900 T, Perkin Elmer, Waltham, MA, USA), respectively. Methods follow those of Page et al. (1982).

The changes in pH (ΔpH), NO_3^--N (ΔNO_3^--N), AP (ΔAP), AK (ΔAK), and Ex-Ca (ΔEx-Ca) were calculated as follows:

$$\Delta pH = pH_{age} - pH_{crop} \quad (1)$$

$$\Delta NO_3^-\text{-}N = NO_3^-\text{-}N_{age} - NO_3^-\text{-}N_{crop} \quad (2)$$

$$\Delta AP = AP_{age} - AP_{crop} \quad (3)$$

$$\Delta AK = AK_{age} - AK_{crop} \quad (4)$$

$$\Delta Ex\text{-}Ca = Ex\text{-}Ca_{age} - Ex\text{-}Ca_{crop} \quad (5)$$

where pH_{crop} and pH_{age} are the soil pH in cropland and apple orchards of different stand ages, respectively. The calculations of ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca followed the same structure.

2.4. Statistical analyses

All statistical analyses were conducted using SPSS 21.0 software (IBM Corp., Armonk, NY, USA). The differences in pH within an identical soil segment were identified using one-way analysis of variance (ANOVA), and a Tukey post-hoc test was subsequently conducted at $p < 0.05$. Fig. 1 was produced using ArcGIS 10.2 (Esri Inc., Redlands, CA, USA), and Origin 2021 (Origin Lab Corp., Northampton, MA, USA) was used for plotting other figures. Partial least squares path modeling (PLS-PM) was performed to examine the possible relations between the changes in and the absolute contents of soil NO_3^--N, AP, AK, and Ex-Ca and soil pH, with the estimates of path coefficients determined using the "pls-pm" package in R software v4.3.3. The model fit was evaluated using the goodness-of-fit (GOF) index (Henseler and Sarstedt, 2013). Aggregated boosting tree models were constructed using the "RandomForest" package in R software to quantify the relative importance of soil NO_3–N, AP, AK, and Ex-Ca in affecting pH and that of ΔNO_3^--N, ΔAP, ΔAK, ΔEx-Ca in affecting ΔpH.

3. Results

3.1. Vertical characteristics of soil pH and ΔpH under different land-use types

Soil pH differed significantly ($p < 0.05$) in the 13-m and 6-m profiles among land-use types. Based on the profile characteristics and differences in soil pH, three soil layers were characterized for each type of orchard as follows: a separating layer: 0–6 m in irrigated and 0–2 m in rainfed orchards; a transitional layer: 6–9 m in irrigated and 2–4 m in rainfed orchards; and an intermixing layer: 9–13 m in irrigated and 4–6 m in rainfed orchards (Fig. 3). Cropland-to-orchard conversion significantly decreased average soil pH across depths by 0.27 units in 25-yr rainfed orchards and by 0.25 units in 30-yr irrigated orchards (Fig. 3b and g). Notably, the depth-averaged pH values were ranked as 8-yr ≈ cropland at 0–2 m and 2–4 m and 8-yr < cropland at 4–6 m in rainfed orchards; whereas in irrigated orchards, pH was not significantly different among cropland and 10- and 20-yr stands at 6–9 m but was

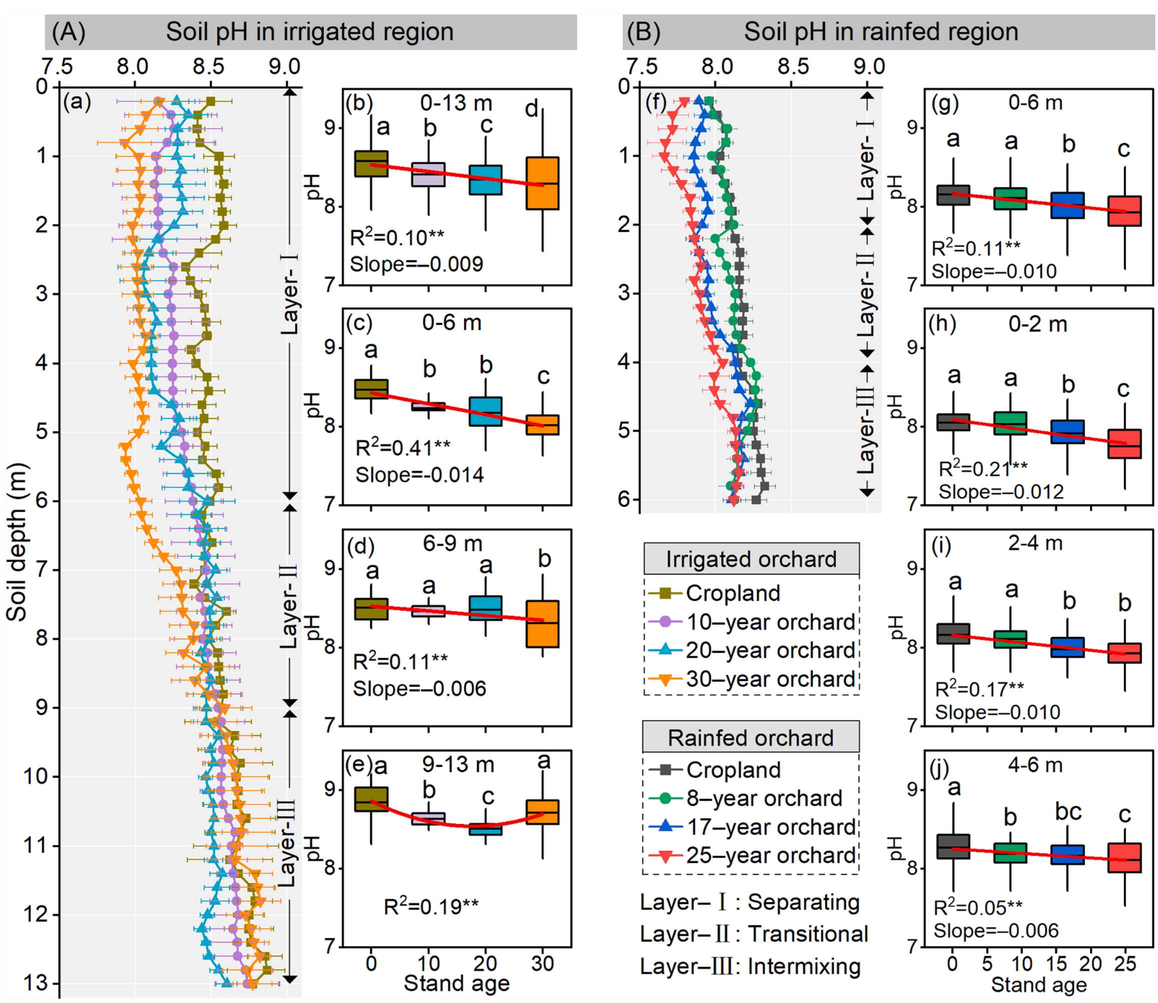

Fig. 3. Vertical distribution patterns of soil pH and the regressions between soil pH and stand age in different soil layers in the irrigated (a-e) and rainfed (f-j) apple-producing regions. Layer–I (separating): 0–6 m in irrigated and 0–2 m in rainfed orchards; Layer–II (transitional): 6–9 m in irrigated and 2–4 m in rainfed orchards; and Layer–III (intermixing): 9–13 m in irrigated and 4–6 m in rainfed orchards. Different lowercase letters indicate significant differences between treatments at $p < 0.05$. *, $p < 0.05$; **, $p < 0.01$.

significantly different between cropland and 10- and 20-yr stands and between 10- and 20-yr stands at 9–13 m (Fig. 3), indicating that soil acidification was most likely to occur in the deepest segment. However, the difference in pH values between cropland and 30-yr orchards was not significant at 9–13 m (Fig. 3e), indicating amelioration of soil acidification. With the exception of 9–13 m, which was well-fitted to a positive quadratic model, soil pH decreased significantly linearly as stand age increased across soil depths. Notably, the slopes of regressions substantially decreased with increasing soil depth. Most importantly, the slope in the 0–6-m layer was higher in irrigated orchards (–0.014) than that in rainfed orchards (–0.010), indicating a faster rate of soil acidification in the irrigated apple production system.

Changes in soil pH (ΔpH) were calculated as the pH value in an apple orchard minus that in cropland for the identical 20-cm layer, and ΔpH showed a clear separation among apple orchards with different stand ages (Fig. 4). The ΔpH values were negative in most cases, indicating soil acidification occurred following cropland-to-orchard conversion. The maximum ΔpH was –0.61 at 5.6–5.8 m in 30-yr irrigated orchards and –0.39 at 0.6–0.8 m in 25-yr rainfed orchards. Notably, ΔpH values were equivalent in the 5–6 m layer across 8-, 17-, and 25-yr rainfed orchards, but ΔpH differed significantly ($p < 0.05$) among 10-, 20-, and 30-yr irrigated orchards to a depth of 7.2 m (Fig. 4), indicating an increase in soil depth of acidification induced by irrigation.

3.2. Changes in soil pH and ΔpH within deep soil profiles

Soil pH significantly linearly increased with increasing soil depth, whether in cropland or apple orchards of different stand ages or in irrigated or rainfed regions (Fig. 5a). By contrast, the change in ΔpH with soil depth was not significant in 8-yr rainfed orchards, and ΔpH was significantly negatively related with soil depth at 8–13-m in the 10- and 20-yr irrigated orchards (Fig. 5b). Thus, changes in cropland indigenous basis of soil pH might mask the real responses of soil pH in deep profiles to orchard stand ages in overfertilized irrigated and rainfed apple production systems. Therefore, an accurate assessment of deep soil acidification should focus on ΔpH values rather than on absolute pH values.

3.3. Regression analysis between soil pH and ΔpH and their potential soil nutrient driving factors

Regression analysis revealed that the relations between soil ΔpH and ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca substantially differed from the relations between soil pH and NO_3^--N, AP, AK, and Ex-Ca irrespective of land-use types and soil layers (Figs. 6 and 7). However, the relationship between soil pH and soil water content (SWC) and between ΔpH and ΔSWC was not significant (Fig. S1). Soil pH was significantly negatively related with NO_3^--N across cropland and apple orchards with different

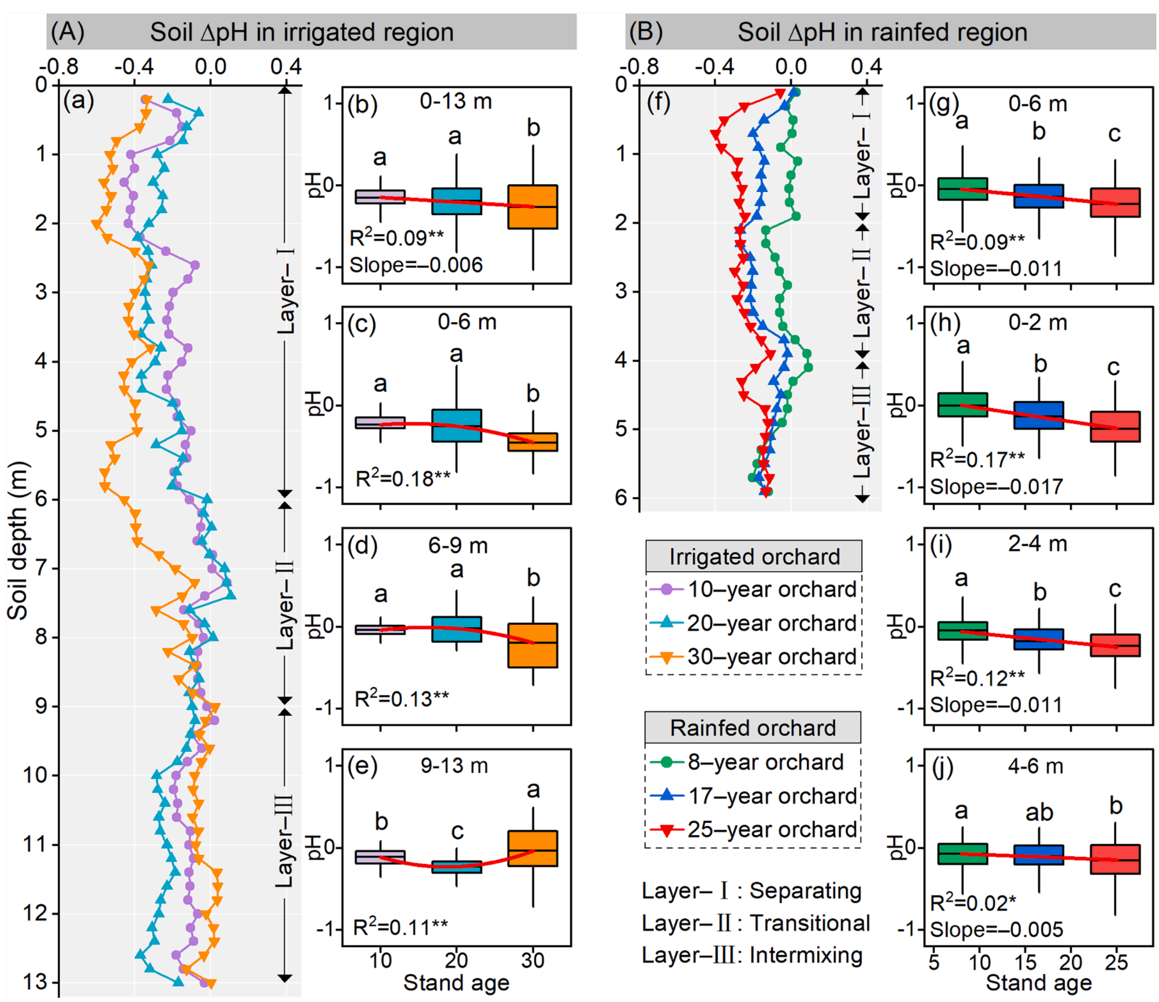

Fig. 4. Vertical distribution patterns of soil ΔpH and the regressions between soil pH and stand age in different soil layers in the irrigated (a-e) and rainfed (f-j) apple-producing regions. Layer–I (separating): 0–6 m in irrigated and 0–2 m in rainfed orchards; Layer–II (transitional): 6–9 m in irrigated and 2–4 m in rainfed orchards; and Layer–III (intermixing): 9–13 m in irrigated and 4–6 m in rainfed orchards. Different lowercase letters indicate significant differences between treatments at $p < 0.05$. *, $p < 0.05$; **, $p < 0.01$.

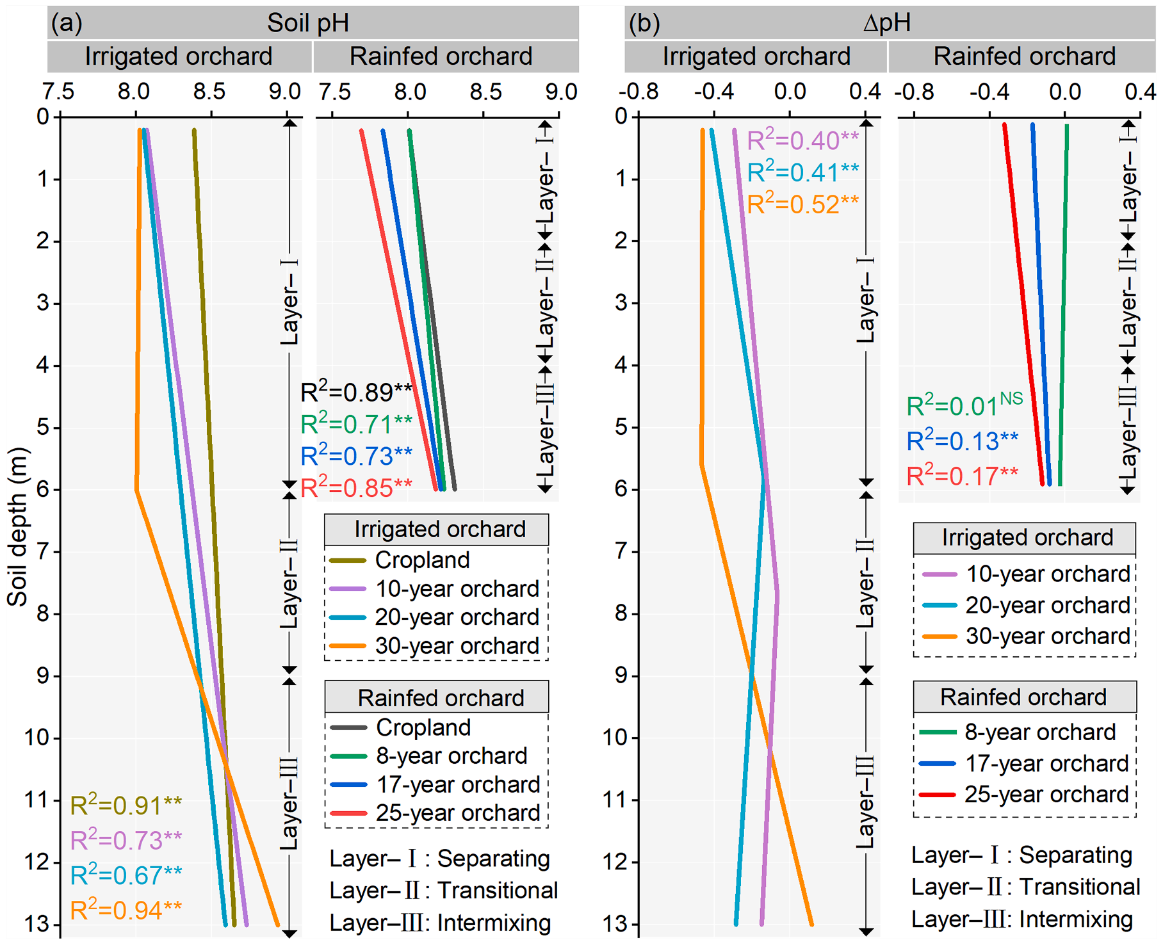

Fig. 5. Linear relationships between soil pH and soil depth (a), and between ΔpH and soil depth (b) in cropland and apple orchards under irrigated and rainfed regions. Layer–I (separating): 0–6 m in irrigated and 0–2 m in rainfed orchards; Layer–II (transitional): 6–9 m in irrigated and 2–4 m in rainfed orchards; and Layer–III (intermixing): 9–13 m in irrigated and 4–6 m in rainfed orchards. *, $p < 0.05$; **, $p < 0.01$.

stand ages in both irrigated and rainfed systems, whereas the relations between ΔpH and ΔNO_3^--N were not significant in 8-yr rainfed orchards and 10-yr irrigated orchards (Fig. 6). In contrast to the nonsignificant relation between AP and soil pH in 30-yr irrigated orchards, the relation between ΔAP and ΔpH was significantly negative in 30-yr in irrigated orchards, as was the relation in 10-yr and 20-yr orchards (Fig. 6b, f). By contrast, soil AP was positively related to pH in cropland and 8-, 17-, and 25-yr apple orchards in the rainfed region, whereas the relation between ΔAP and ΔpH was only significant in 25-yr apple orchards. The relations between soil pH and AK and between ΔpH and ΔAK were not significant across land-use types in irrigated and rainfed regions. In contrast to the negative relation between soil pH and Ex-Ca in 10-yr irrigated orchards, ΔpH was positively related to ΔEx-Ca in 10- and 20-yr orchards. Notably, soil pH significantly decreased with increasing Ex-Ca, and the negative relations between ΔpH and ΔEx-Ca were significant in 30-yr irrigated orchards and 25-yr rainfed orchards (Fig. 6).

There were negative relations between soil pH and NO_3^--N and between ΔpH and ΔNO_3^--N across the three soil layers in irrigated and rainfed regions (Fig. 7). Results were similar for AP and ΔAP at 0–6 m in the irrigated region and at 0–2 m in the rainfed region, whereas the relation was positive for AP and ΔAP at 9–13 m in the irrigated region and for AP at 2–4 m in the rainfed region (Fig. 7). A positive relation between ΔAK and ΔpH was recorded at 0–6 m in the irrigated region and 4–6 m in the rainfed region. At 4–6 m in the rainfed region, soil pH significantly decreased with increasing Ex-Ca, but the relation between ΔpH and ΔEx-Ca was not significant at 9–13 m in the irrigated region (Fig. 7). There were significantly positive relations between soil pH and Ex-Ca and between ΔpH and ΔEx-Ca in the 0–6 m in the irrigated region, whereas the corresponding relations were significantly negative in the 0–2 m in the rainfed region. Notably, soil pH was negatively related to Ex-Ca in both irrigated and rainfed systems, whereas ΔpH and ΔEx-Ca were negatively related in rainfed orchards but positively related in irrigated orchards (Fig. 7).

3.4. Partial least squares path models

Topsoils, rather than subsoils, can better characterize soil biochemical processes induced by concurrent plant growth and anthropogenic activity (e.g., fertilization) (Huang et al., 2023). Given that soil NO_3^--N, AP, AK, and Ex-Ca exerted greater influence on soil pH at 9–13 m than at 0–6 m in the irrigated region and at 4–6 m than at 0–2 m in the rainfed region (Fig. 8), PLS-PM analysis was used to elucidate the effects of changes in soil available N, P, K and Ca on soil acidification (Fig. 9). In the irrigated apple-producing region at 0–6 m, ΔNO_3^--N and ΔAP negatively regulated but ΔAK and ΔEx-Ca positively mediated ΔpH (Fig. 9a). Similar intrarelations were observed when all data were pooled (Fig. 9d). By contrast, at depths of 6–9 m and 9–13 m, ΔNO_3^--N, but not ΔAP, ΔAK, and ΔEx-Ca, significantly negatively influenced ΔpH (Fig. 9b and c). In the rainfed apple-producing region, ΔpH was negatively affected by ΔNO_3^--N, ΔAP, and ΔAK at 0–2 m and by ΔNO_3^--N at at 2–4 and 4–6 m, and ΔEx-Ca had a positive effect on ΔpH at 2–4 m (Fig. 9). Soil ΔNO_3^--N but not ΔAP, ΔAK, and ΔEx-Ca negatively regulated ΔpH over the entire 0–6-m profile (Fig. 9i). According to aggregated boosted tree analysis of pooled data, ΔNO_3^--N was the most

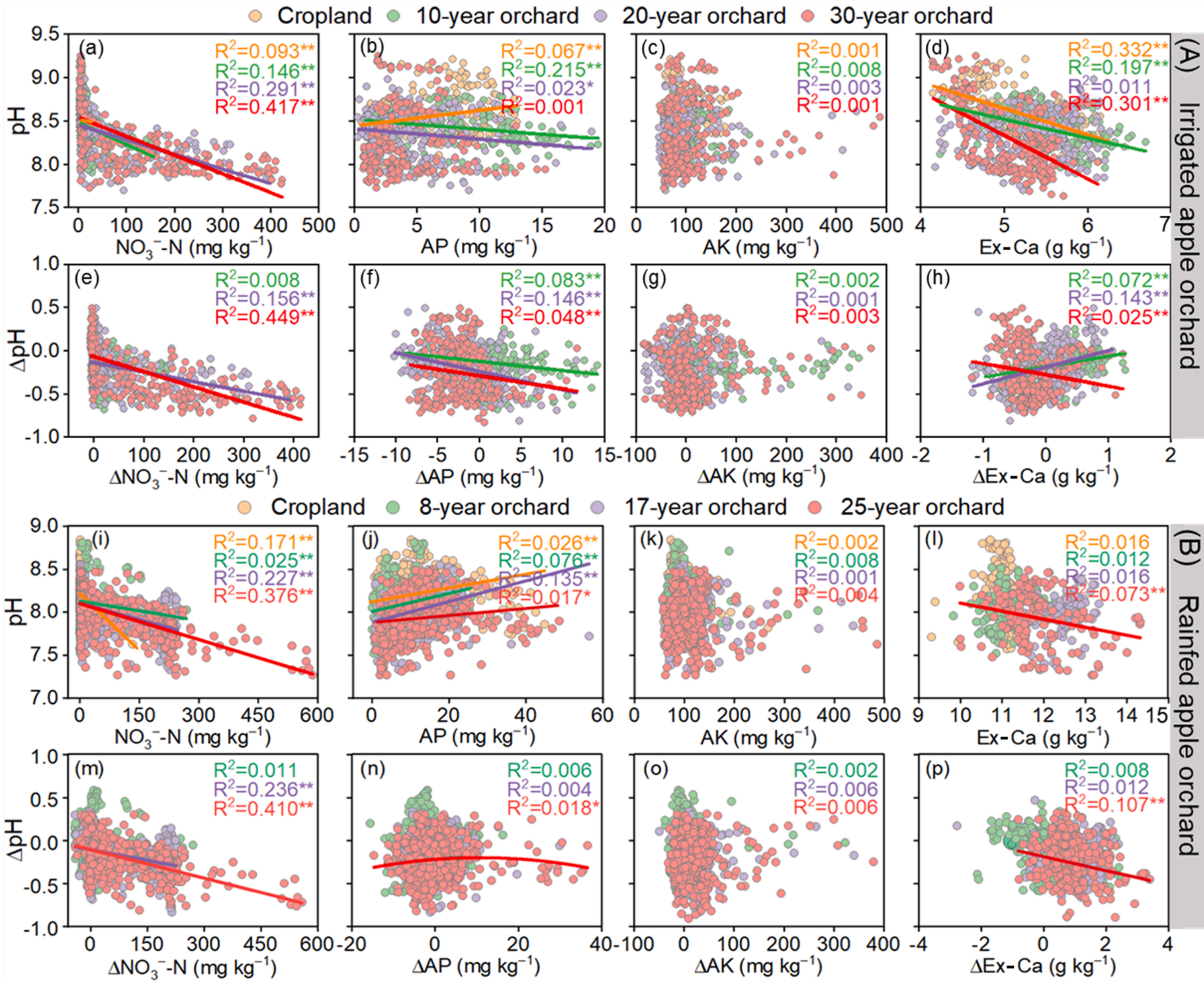

Fig. 6. Regression analysis between pH and NO_3^--N, AP, AK, and Ex-Ca, and between ΔpH and ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca under different land-use types in irrigated (A) and rainfed (B) apple-producing regions. *, $p < 0.05$; **, $p < 0.01$.

important factor affecting ΔpH, followed by ΔAP, ΔEx-Ca, and ΔAK in the irrigated apple-producing region (Fig. 9e). Similarly, in the rainfed region, ΔNO_3^--N was the most important factor, followed by ΔEx-Ca, ΔAP, ΔAK (Fig. 9j).

4. Discussion

4.1. Changes in soil pH in deep soil profiles in irrigated and rainfed apple orchards

Severe declines in soil pH are reported at 0–0.2-m and 0–6-m depths in rainfed apple-producing systems on the Loess Plateau (Hou et al., 2021; Zhao et al., 2024). In this study, we provide new evidence that soil acidification occurred in deep profiles in irrigated apple orchards. Consistent with the findings obtained by Zhang et al. (2017) and Ren et al. (2023), soil pH generally increased with increasing soil depth in both rainfed cropland and orchard systems, and orchard-induced declines in pH decreased as soil depth increased (Fig. 3). Results were similar in the irrigated region except in 30-yr irrigated orchards, which had a constant pH value of ~8.0 across the 0–6 m of soil profile, likely attributed to irrigation-induced leaching loss of base cations (Li et al., 2024). Such leaching of base cations might partially explain the higher annual acidification rate in the irrigated region (slope = –0.014) than that in the rainfed region (slope = –0.010). Land-use change significantly affects the vertical distribution of soil pH in deep profiles (Brasseur et al., 2018). Nitrogen loading is responsible for soil acidification (Guo et al., 2010), and the sampling depths of 6 m in the rainfed region and 13 m in the irrigated region were chosen in this study because they were sufficient to assess NO_3^--N dynamics, according to Liu et al. (2019) and Zhu et al. (2022). However, the significant differences in soil pH at 5.8–6.0 m indicated that a 6-m profile was insufficient for evaluating pH dynamics in rainfed apple production systems. This result is in contrast to the findings of Ren et al. (2023), who found nonsignificant differences in soil pH between cropland and apple orchards below 6 m, which may, however, be due to the insufficient number of sampling replicates ($n = 3$). Similarly, due to differences among stand ages at the 13 m depth, a 13-m profile was not sufficiently robust for exploring orchard-induced changes in soil pH in the irrigated region (Fig. 3), which was most likely due to the deep root systems of apple trees, which can extend to 18 m (Wang et al., 2015b). Undoubtedly, the depth of soil acidification was deeper in irrigated orchards than in rainfed orchards, which was most likely related to the sandy soils on the Loess Plateau exacerbating the leaching of base cations due to flood-irrigation and overfertilization (Sigler et al., 2020).

The results indicated that cropland-to-orchard conversion would result in declines in soil pH in deep profiles in both irrigated and rainfed

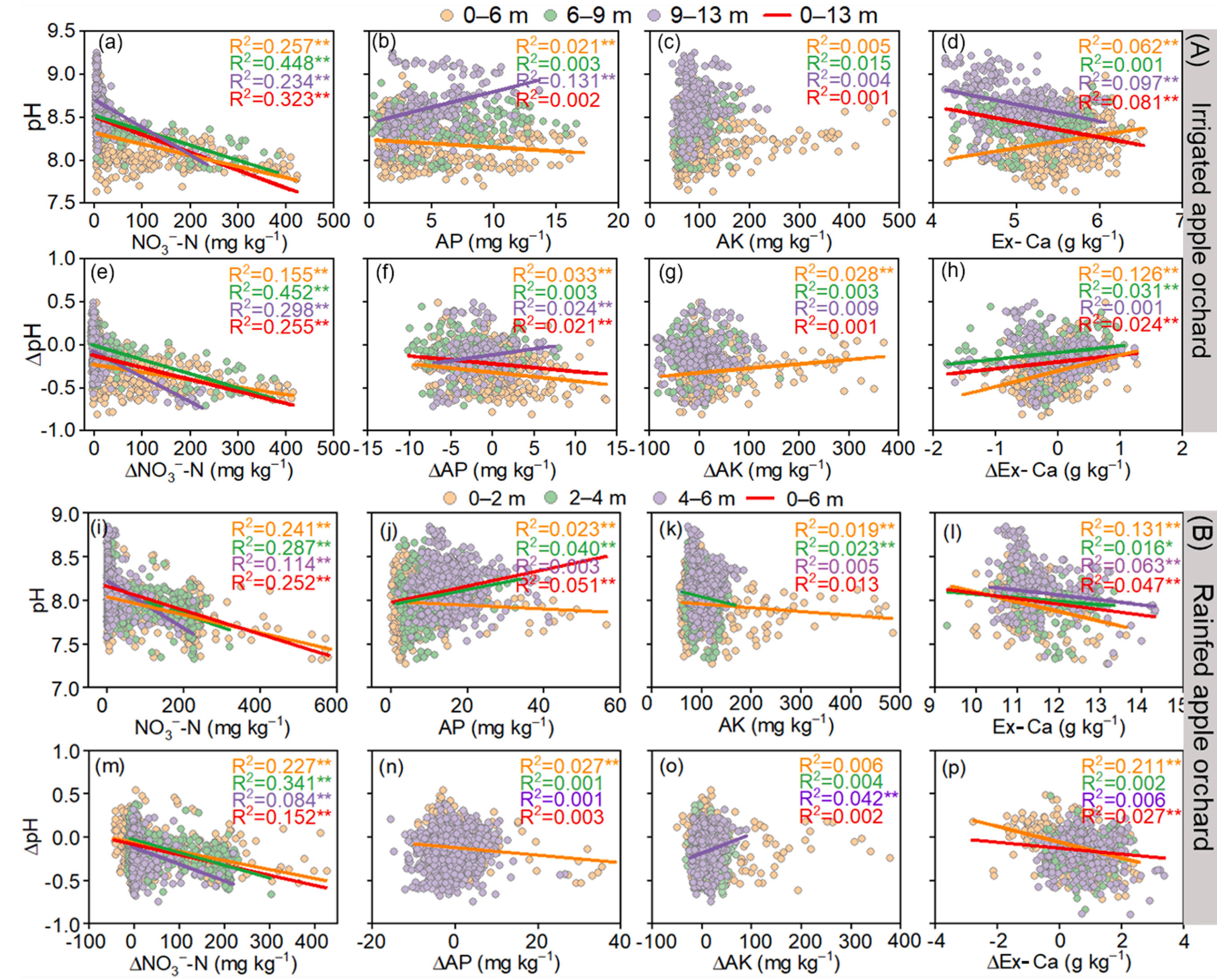

Fig. 7. Regression analysis between pH and NO_3^--N, AP, AK, and Ex-Ca, and between ΔpH and ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca under different soil layers in irrigated (A) and rainfed (B) apple-producing regions. *, $p < 0.05$; **, $p < 0.01$.

orchards, with soil acidification aggravated by increasing stand age (Fig. 3). Over-fertilization has led to a massive accumulation of nitrates in the soil profile of both irrigated and rainfed apple orchards (Zhu et al., 2022). However, the differences in soil NO_3^--N at 5–6 m in the rainfed region and at 8–13 m in irrigated region were not significant between cropland and 20-yr apple orchards (Liu et al., 2019; Zhu et al., 2022). Accordingly, soil NO_3^--N did not adequately explain the pH decline at 5–6 m in 17-yr rainfed orchards and at 10–13 m in 20-yr irrigated orchards. We collected data on soil pH and NO_3^--N at 6–10 m from Ren et al. (2023) and found a similar result after a regression analysis. $NH_4H_2PO_4$ and K_2SO_4 were the main sources of phosphate and potassium, both of which were physiologically acidic (Hu and Zhou, 2003). Soil acidification can occur due to the release of H^+ during the dissolution of $H_2PO_4^-$ in water and the replacement of Ca^{2+} by K^+ in alkaline soils (Wang et al., 2015a; Schneider and Mollier, 2016). Furthermore, AP and AK are important indicators for assessing soil acidification (Zeng et al., 2017; Lv et al., 2020). Considering the calcium-buffering systems of calcareous soils (Raza et al., 2020), we should examine other soil properties, such as AP, AK, and Ex-Ca, in identifying factors affecting soil acidification. Equally important, the contrasting changes in pH and ΔpH with soil depth in young apple orchards (≤10 years) suggested that the changes in soil pH values rather than the absolute values best quantified soil acidification (Fig. 5). Therefore, the initial values of cropland as a control were subtracted, and the observed changes in key driving factors were then used for calculating their contributions to soil acidification.

4.2. Comparisons of the relations between soil pH and ΔpH and potential driving factors

Soil pH increased as soil depth increased (Fig. 3; Wang et al., 2022), whereas soil nutrients decrease with increasing depth (Zhao et al., 2024). Those results might partially explain the negative relations between soil pH and NO_3^--N, AP, AK, and Ex-Ca across land-use types and soil depths (Figs. 6 and 7). Hence, there was a numerical rather than a causal relation when the absolute values of soil properties were used in regression analysis. There are significant differences in cumulative N–P_2O_5–K_2O inputs and nutrient uptake between cropland and apple orchards of different tree ages and thus contrasting soil physicochemical properties in deep profiles (De et al., 2012). Therefore, the relations between soil pH and ΔpH and their potential driving factors were analyzed in each land-use type (Fig. 6). Consistent with Zhao et al. (2023), our study found no significant relationships between SWC and pH, or between ΔSWC and ΔpH (Fig. S1). The relations between ΔpH and ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca were substantially different from those between pH and NO_3^--N, AP, AK, and Ex-Ca. In contrast to the

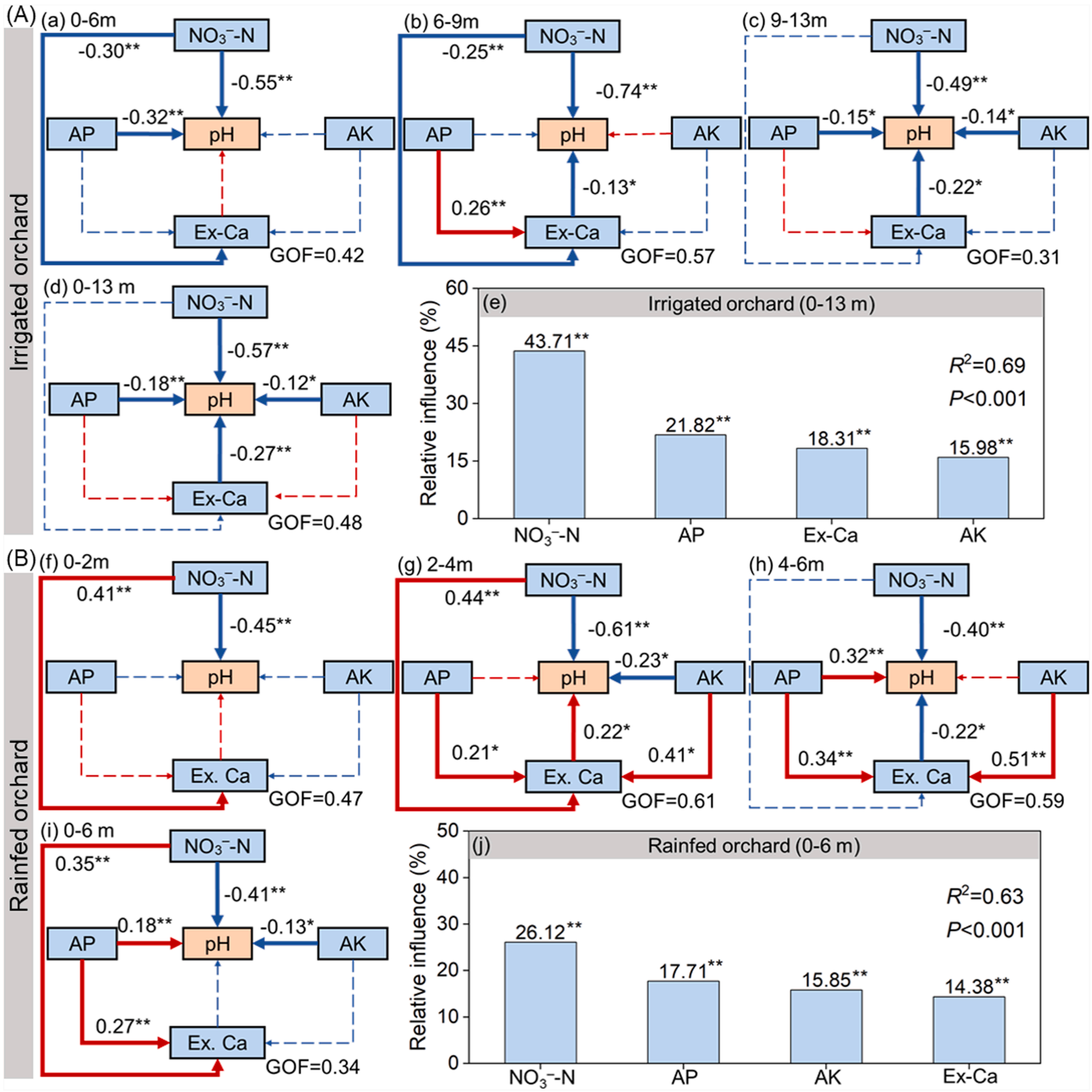

Fig. 8. Partial least squares path model illustrating the direct and indirect effects of NO_3^--N, AP, AK, and Ex-Ca on soil pH, and aggregated boosted tree analysis depicting the relative influence of NO_3^--N, AP, AK, and Ex-Ca on soil pH in irrigated (A) and rainfed (B) apple-producing regions. Blue and red arrows indicate positive and negative flows of causality, respectively. Dashed arrows denote no causal relationship between the two variables. Numbers with arrows represent significant standardized path coefficients. *, $p < 0.05$; **, $p < 0.01$.

significant and negative relations between soil pH and NO_3^--N across cropland and orchards in both irrigated and rainfed regions, the relations between ΔpH and ΔNO_3^--N were not significant in 10-yr irrigated orchards and 8-yr rainfed orchards. Considering the nonsignificant changes in pH in 8-yr rainfed orchards compared with cropland (Fig. 5), we concluded that the changes in rather than the absolute values of NO_3^--N explained the soil acidification. In contrast to the absence of a relation between AP and soil pH in 30-yr irrigated orchards, that between ΔpH and ΔAP was significant in 30-yr irrigated orchards, indicating that ΔAP but not AP helped explain soil acidification. Soil AP increased, but there were no significant differences in the 0.4–6-m layer between cropland and 8-, 17-, and 25-yr apple orchards in the rainfed region (Liu et al., 2021), implying that the significant and positive relations between soil pH and AP were not causal. The changes in soil AP and pH will become more obvious over time (Johnston and Poulton, 2018), which might explain the significant relations between ΔpH and ΔAP in 25-yr but not in 8-yr and 17-yr rainfed orchards. The nonsignificant relations between AK and pH and between ΔAK and ΔpH irrespective of land-use types and study regions were primarily ascribed to the high indigenous levels of soil AK and only slight changes induced by K fertilization (Hou et al., 2021). The most severe soil acidification occurred in the older orchards and accelerated the dissolution of $CaCO_3$ (Raza et al., 2020), which was the primary reason for the negative relations between soil pH and Ex-Ca and ΔpH and ΔEx-Ca in 25-yr rainfed

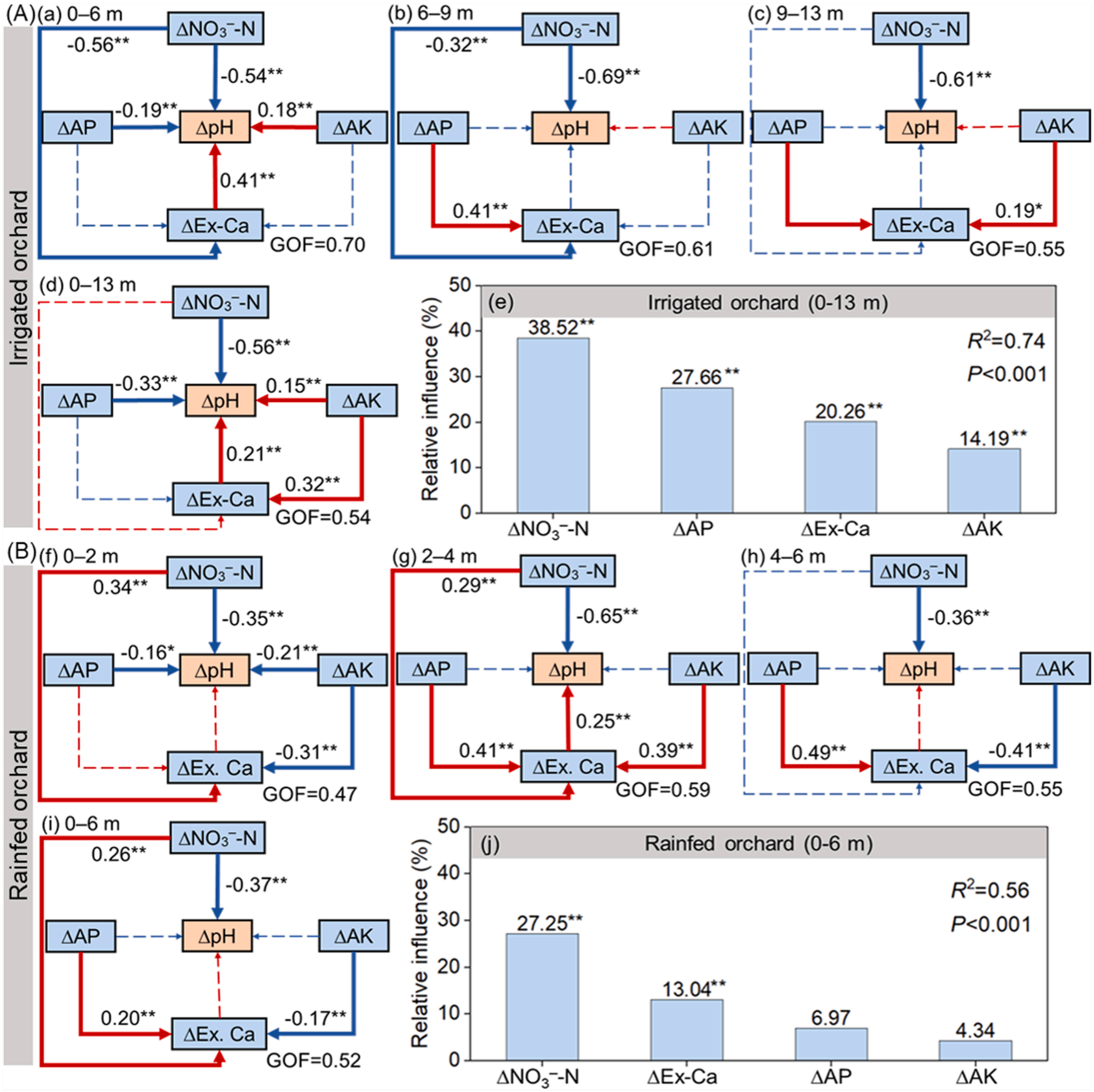

Fig. 9. Partial least squares path model illustrating the direct and indirect effects of ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca on ΔpH, and aggregated boosted tree analysis depicting the relative influence of ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca on ΔpH, in irrigated (A) and rainfed (B) apple-producing regions. Blue and red arrows indicate positive and negative flows of causality, respectively. Dashed arrows denote no causal relationship between the two variables. Numbers with arrows represent significant standardized path coefficients. *, $p < 0.05$; **, $p < 0.01$.

orchards and 30-yr irrigated orchards. The opposite vertical distributions of soil pH and Ex-Ca explained the negative relation between Ex-Ca and pH in cropland. Irrigation-induced calcium migration to deeper soil layers may explain the decrease in coefficient of determination (R^2) of the regressions between Ex-Ca and pH in 10-yr and 20-yr irrigated orchards (Li et al., 2024). By contrast, the positive relations between ΔpH and ΔEx-Ca in 10-yr and 20-yr irrigated orchards were most likely associated with the Ca lixiviation resulting from exchanges on the cation exchange capacity with protons (H^+), and its subsequent enhancement of $CaCO_3$ buffer systems, according to Aquilina et al. (2012). The significant relation between ΔpH and ΔEx-Ca in 20-yr irrigated orchards partially supported the hypothesis that ΔEx-Ca rather than Ex-Ca would explain soil acidification.

Soil physicochemical properties vary greatly across deep soil profiles (Brasseur et al., 2018), although such background information is always ignored when factor analysis is conducted to quantify the effects of land-use changes (Ren et al., 2023). In this study, the significant negative relations between ΔpH and ΔNO_3^--N across soil depths in irrigated and rainfed regions provides new evidence for the consensus that soil NO_3^--N is responsible for soil acidification. Because the relations between ΔpH and ΔNO_3^--N in 10-yr irrigated orchards and 8-yr rainfed orchards were not significant, we used the data obtained from 20- and 30-yr orchards in the irrigated region and 17- and 25-yr orchards in the rainfed region for factor analysis (Fig. 8). The R^2 value and the slope were higher for the relation between pH and NO_3^--N than that between ΔpH and ΔNO_3^--N (Fig. 6), implying that the importance of NO_3^--N in explaining soil acidification is overestimated. Han et al. (2020) reported that AP negatively affects soil pH in major Chinese croplands. Phosphorus fertilization substantially changes topsoil AP compared with that in subsoil (Liu et al., 2021), which could explain the negative relations between AP and pH and ΔAP and ΔpH in the 0–6-m depth in the irrigated region and the 0–2-m depth in the rainfed region (Fig. 7). The higher R^2 value between ΔAP and ΔpH than that between AP and pH could be attributed to the lower variation across the 6-m and 13-m profiles. This result might also explain the significant negative relation between ΔAP and soil acidity, but not that for AP and soil acidity, in the 0–13-m soil profile (Fig. 7f). Those results indicated that ΔAP was more accurate than AP in predicting soil acidification. The removal of base cations is another driver of soil acidification (Guo et al., 2010). Potassium fertilization substantially alleviated the irrigation-induced leaching of base cations, thereby contributing to the significant positive relation between ΔAK and ΔpH at 0–6 m in the irrigated region. Similarly, fertilizer-K leaching along pores of the root–soil interface significantly increases AK at the 4–6 m depth in 17- and 25-yr orchards (Zhao et al., 2024), which might explain the significant positive relations between ΔAK and ΔpH at 4–6 m in the rainfed region. The K-leaching rate decreases with increasing soil pH, which was another reason for the positive relation between ΔAK and ΔpH at 0–6 m in the irrigated region and at 4–6 m in the rainfed region, according to Fatemi (2017). Furthermore, our results indicated that the relations between ΔpH and ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca were substantially different from those between pH and NO_3^--N, AP, AK, and Ex-Ca. However, most existing studies focus only on the relationship between absolute values and soil acidification, while analyzing changes in these values may provide additional insights.

4.3. Irrigation effects on the relations between soil pH and potential driving factors

The significant negative relations between ΔNO_3^--N and ΔpH and between NO_3^--N and pH across soil depths in both irrigated and rainfed regions support the consensus that the overapplication of N fertilizers is the most important driver of soil acidification in China (Zeng et al., 2017). Irrigation potentially complicates soil acidification processes because it promotes nutrient migration to deep soil layers (Raza et al., 2020; Li et al., 2024). At the identical depth of 0–6 m, ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca significantly regulated ΔpH in the irrigated region, whereas ΔNO_3^--N was the unique factor negatively affecting ΔpH in the rainfed region (Fig. 9a and i), providing new evidence that irrigation can increase the relations between ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca and soil acidification. Notably, the effects of ΔAK on ΔpH changed from negative to positive after irrigation, and irrigation also increased the contribution of ΔAP but not that of ΔEx-Ca to soil acidification (Fig. 9). Therefore, soil AP and AK, as indicators of P and K fertilizers, should be considered for a full understanding soil acidification processes, especially in irrigated farming systems. The responses of soil properties to fertilization and irrigation are greater in topsoil than in subsoil (He et al., 2023). However, the interrelations among pH, NO_3^--N, AP, AK, and Ex-Ca typically increased with soil depth, which partially supported that changes were more accurate than absolute values in predicting the key factors driving soil acidification (Figs. 8 and 9).

4.4. Uncertainties and implications

This study focused on comparing the relations between the absolute values of and the changes in soil pH and the potential drivers of soil available N, P, K, and Ca. The results highlight the importance of the changes in soil available N, P, K, and Ca to provide more accurate explanations of soil acidification in deep soil profiles induced by land-use changes. Unfortunately, we failed to establish theoretical calculations of the equivalence between AP/AK and protons, according to Guo et al. (2010). In contrast to the cereal croplands, the contributions of AP and AK to soil acidification were detectable because of the extreme overfertilization in apple orchards, which may be the major reason why AP and AK are neglected in addressing soil acidification in earlier works (Guo et al., 2010; Zeng et al., 2017). Moreover, the contributions of ΔNO_3^--N, ΔAP, ΔAK, and ΔEx-Ca to soil acidification were age-dependent, and thus, soil sampling from apple orchards with additional stand ages is required to comprehensively assess soil acidification in apple production systems. The Loess Plateau has thick loess deposits and thereby provides an ideal platform to investigate vertical characteristics of pH in deep soils. The absence of stabilized soil pH to a depth of 13 m in irrigated orchards and to a depth of 6 m in rainfed orchards indicated soil acidification was underestimated, suggesting that to better understand of acidification, soil samples need to be collected in deeper soil profiles in future studies. The uptake of base cations (e.g., Ca^{2+} and K^+) by the deep roots of apple trees also significantly affects soil pH in deeper soil layers (Hinsinger et al., 2003; Droue et al., 2015). Such biotic factors were not taken into account in this study. Over-fertilization and soil acidification have resulted in the massive accumulation of NO_3^--N in the soil profiles, the loss of soil inorganic carbon, and increased greenhouse gas emissions, threatening apple production in the Loess Plateau (Raza et al., 2020; Han et al., 2023; Zhao et al., 2023). To mitigate soil acidification of apple production systems in China, it is urgent to reduce the rampant overfertilization by farmers with chemical N–P_2O_5–K_2O fertilizers of 1200–675–900 kg ha^{-1} yr^{-1}.

5. Conclusion

Cropland-to-orchard conversion resulted in severe soil acidification in deep profiles in rainfed and irrigated apple-producing regions of the Loess Plateau. In addition to NO_3^--N, soil AP, AK, and Ex-Ca also significantly regulated soil acidification, and their contributions differed considerably between rainfed and irrigated regions. When the relations between soil pH and ΔpH and soil available N, P, K, and Ca were compared, we found that ΔpH was more effective than pH in visually reflecting deep soil acidification, and thus, the changes in rather than the absolute values of soil available N, P, K, and Ca provided more accurate explanations for soil acidification. Notably, such conclusions were significantly affected by soil depth, irrigation, and orchard age, indicating that further studies are needed to determine the reliability of our results. Importantly, irrigation accelerated soil acidification. This study provides an early warning on deep soil acidification in apple production systems, and the excessive application of chemical N–P_2O_5–K_2O fertilizers must be controlled to reconcile apple production and soil quality.

CRediT authorship contribution statement

Xinpeng Xu: Supervision, Resources, Methodology. **Chao Ai:** Validation, Supervision, Resources, Methodology. **Yuanjun Zhu:** Validation, Software, Methodology, Formal analysis. **Zhanjun Liu:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Funding acquisition. **Shilong Sun:** Validation, Resources, Formal analysis, Data curation, Conceptualization. **Haotian Shi:** Writing – review & editing, Writing – original draft, Validation, Software, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Zhaohui Wang:** Visualization, Supervision, Funding acquisition.

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.

Acknowledgments

This work was supported by the National Key Research & Development Program of China (2021YFD1900703), the earmarked fund for the Apple Modern Agro-industry Technology Research System (CARS-27), and the Major Science and Technology Projects in Shaanxi Province (2020zdzx03–02–01).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2025.109863.

Data Availability

Data will be made available on request.

References

Aquilina, L., Poszwa, A., Walter, C., Vergnaud, V., Pierson–Wickmann, A.C., Ruiz, L., 2012. Long–term effects of high nitrogen loads on cation and carbon riverine export in agricultural catchments. Environ. Sci. Technol. 46 (17), 9447–9455. https://doi.org/10.1021/es301715t.

Brasseur, B., Spicher, F., Lenoir, J., Gallet-Moron, E., Buridant, J., Horen, H., 2018. What deep-soil profiles can teach us on deep-time pH dynamics after land use change? Land Degrad. Dev. 29, 2951–2961. https://doi.org/10.1002/ldr.3065.

Chen, M.Y., Shao, M.A., Wei, X.R., Li, T.C., Shen, N., Mi, M.X., Zhao, C.L., Yang, X., Gan, M., Bai, X., Li, A., 2022. Response of the vertical distribution of soil water and nitrogen in the 5 m soil layer to the conversion of cropland to apple orchards in the Loess Plateau, China. Agric. Ecosyst. Environ. 333, 107960. https://doi.org/10.1016/j.agee.2022.107960.

De, S.A., De Frenne, P., Staelens, J., Verstraeten, G., Muys, B., Vesterdal, L., 2012. Tree species traits cause divergence in soil acidification during four decades of post agricultural forest development. Glob. Change Biol. 18, 1127–1140. https://doi.org/10.1111/j.1365–2486.2011.02572.x.

Droue, T., Herbauts, J., Demaiffe, D., 2015. Influence of deep soil horizons on Ca nutrition of forest stands along a loessic soil sequence. Plant Soil 394, 373–389. https://doi.org/10.1007/s11104–015–2540–3.

FAO and ITPS, 2015. Status of the World's Soil Resources (SWSR)—Main Report. Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils, Rome, Italy. ⟨http://www.fao.org/3/a⟩–i5199e.pdf.

FAOSTAT, 2022. Statistics Division. Food and Agriculture Organization of the United Nations. ⟨http://www.fao.org/faostat/en/#data⟩.

Fatemi, A., 2017. Kinetics of soil potassium release under long–term imbalanced fertilization in calcareous soils. Pedosphere 27 (6), 1105–1115. https://doi.org/10.1016/S1002–0160(17)60380–1.

Ge, S.F., Zhu, Z.L., Jiang, Y.M., 2018. Long–term impact of fertilization on soil pH and fertility in an apple production system. J. Soil Sci. Plant Nut 18 (1), 282–293. https://doi.org/10.4067/S0718–95162018005001002.

Guo, J.H., Liu, X.J., Zhang, Y., Shen, J.L., Han, W.X., Zhang, W.F., Christie, P., Goulding, K.W.T., Vitousek, P.M., Zhang, F.S., 2010. Significant acidification in major Chinese croplands. Science 327, 1008–1010. https://doi.org/10.1126/science.1182570.

Han, J.L., Jin, X.L., Huang, S.W., Zhu, X.Y., Liu, J.J., Chen, J.Y., Zhang, A.F., Wang, X.D., Tong, Y.A., Hussain, Q., Feng, H., 2023. Carbon and nitrogen footprints of apple orchards in China's Loess Plateau under different fertilization regimes. J. Clean. Prod. 413, 137546. https://doi.org/10.1016/j.jclepro.2023.137546.

Han, T.F., Liu, L.K., Huang, J., Ma, B.C., Zheng, L., Wang, H.Y., Qu, X.L., Ren, Y., Yu, Z. K., Zhang, H.M., 2020. Spatio–temporal evolution of soil pH and its driving factors in the main Chinese farmland during past 30 years. J. Plant Nutr. Fertil. 26 (12), 2137–2149. https://doi.org/10.11674/zwyf.20399.

He, H.R., Zhou, J.X., Wang, Y.Q., Jiao, S., Qian, X., Liu, Y.R., Liu, J., Chen, J., Delgado–Baquerizo, M., Brangarí, A.C., Chen, L., Cui, Y.X., Pan, H.B., Tian, R.M., Liang, Y.T., Tan, W.F., Ochoa–Hueso, R., Fang, L.C., 2023. Deciphering microbiomes dozens of meters under our feet and their edaphoclimatic and spatial drivers. Glob. Change Biol. 00, e17028. https://doi.org/10.1111/gcb.17028.

Henseler, J., Sarstedt, M., 2013. Goodness-of-fit indices for partial least squares path modeling. Comput. Stat. 28 (2), 565–580. https://doi.org/10.1007/s00180-0120317-1.

Hinsinger, P., Plassard, C., Tang, C.X., Jaillard, B., 2003. Origins of root–mediated pH changes in the rhizosphere and their responses to environmental constraints: a review. Plant Soil 248, 43–59. https://doi.org/10.1023/A:1022371130939.

Hou, L.Y., Liu, Z.J., Zhao, J.R., Ma, P.Y., Xu, X.P., 2021. Comprehensive assessment of fertilization, spatial variability of soil chemical properties, and relationships among nutrients, apple yield and orchard age: a case study in Luochuan County, China. Ecol. Indic. 122, 107285. https://doi.org/10.1016/j.ecolind.2020.107285.

Hu, A.T. (Ed.), & Zhou, L. X. (Assoc. Ed.), 2003. Plant Nutrition (Volume 2) (2nd ed.). China Agricultural University Press.

Huang, W.G., Kuzyakov, Y., Niu, S.L., Luo, Y., Sun, B., Zhang, J.B., Liang, Y.T., 2023. Drivers of microbially and plant–derived carbon in topsoil and subsoil. Driv. Microb. PlantDeriv. Carbon Topsoil Subsoil. Glob. Change Biol. 29, 6188–6200. https://doi.org/10.1111/gcb.16951.

IUSS Working Group WRB, 2014. World Reference Base for soil resources 2014. In: International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports. No. 106. FAO, Rome.

Johnston, A.E., Poulton, P.R., 2018. The importance of long–term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience. Eur. J. Soil Sci. 69 (1), 113–125. https://doi.org/10.1111/ejss.12521.

Li, Y.J., Li, Z.J., Gong, P., He, X.L., Liu, H.G., Li, L., Wang, C.X., Li, P.F., Wei, J., Yu, X.Y., 2024. Enhanced irrigation volume reduces salinity and improves deep root zone soil nutrients, phosphatase activity and changes root traits of fruit trees. Agric. Water Manag 302, 109001. https://doi.org/10.1016/j.agwat.2024.109001.

Liu, Z.J., Hou, L.Y., Zhu, Y.J., Xu, X.P., 2021. Vertical distribution and regulation of Olsen–phosphorus in 6–m soil profiles after farmland–to–apple orchard conversion on the Chinese Loess Plateau. Catena 202, 105254. https://doi.org/10.1016/j.catena.2021.105254.

Liu, Z.J., Ma, P.Y., Zhai, B.N., Zhou, J.B., 2019. Soil moisture decline and residual nitrate accumulation after converting cropland to apple orchard in a semiarid region: evidence from the Loess Plateau. Catena 181, 104080. https://doi.org/10.1016/j.catena.2019.104080.

Lv, H.F., Zhao, Y.M., Wang, Y.F., Wan, L., Wang, J.G., Butterbach–Bahl, K., Lin, S., 2020. Conventional flooding irrigation and over fertilization drives soil pH decrease not only in the top– but also in subsoil layers in solar greenhouse vegetable production systems. Geoderma 363, 114156. https://doi.org/10.1016/j.geoderma.2019.114156.

NBSC, 2022. National Bureau of Statistics of China. National Database. China Statistical Yearbook. China Statistical Press, Beijing. ⟨http://www.stats.gov.cn/tjsj/nd⟩.

Page, A.L., Miller, R.H., Keeney, D.R., 1982. Methods of Soil. Analysis, 2nd edn. American Society of Agronomy, Madison, WI.

Raza, S., Miao, N., Wang, P.Z., Ju, X.T., Chen, Z.J., Zhou, J.B., Kuzyakov, Y., 2020. Dramatic loss of inorganic carbon by nitrogen–induced soil acidification in Chinese croplands. e7–e10 Glob. Change Biol. 27. https://doi.org/10.1111/gcb.15101.

Ren, M., Li, C.J., Gao, X.D., Niu, H.H., Cai, Y.H., Wen, H.X., Yang, M.H., Siddique, K.H. M., Zhao, X.N., 2023. High nutrients surplus led to deep soil nitrate accumulation and acidification after cropland conversion to apple orchards on the Loess Plateau, China. Agric. Ecosyst. Environ. 351, 108482. https://doi.org/10.1016/j.agee.2023.108482.

Rezapour, S., Asadzadeh, F., Heidari, M., 2024. Comparative assessment of soil health attributes between topsoil and subsoil influenced by long–term wastewater irrigation. Agric. Water Manag 302, 109012. https://doi.org/10.1016/j.agwat.2024.109012.

Schneider, A., Mollier, A., 2016. Modelling of K/Ca exchange in agricultural soils. Geoderma 271, 216–224. https://doi.org/10.1016/j.geoderma.2016.02.016.

Sigler, W.A., Ewing, S.A., Jones, C.A., Payn, R.A., Miller, P., Maneta, M., 2020. Water and nitrate loss from dryland agricultural soils is controlled by management, soils, and weather. Agric. Ecosyst. Environ. 304, 107158. https://doi.org/10.1016/j.agee.2020.107158.

Tian, D.S., Niu, S.L., 2015. A global analysis of soil acidification caused by nitrogen addition. Environ. Res. Lett. 10, 024019. https://doi.org/10.1088/1748–9326/10/2/024019.

Wang, J.D., Xu, X.J., Ning, Y.W., Zhang, H., Ma, H.B., Zhang, Y.C., 2015a. Research progress on the main agricultural drivers of accelerated soil acidification. Soils 47 (4), 627–633. https://doi.org/10.13758/j.cnki.tr.2015.04.001.

Wang, X.Y., Tong, Y.A., Liu, F., Zhao, Z.P., 2013. Evaluation of the situation of fertilization in apple fields in Shaanxi province. J. Plant Nutr. Fertil. 19, 206–213.. https://doi.org/10.11674/zwyf.2013.0125.

Wang, Y.Q., Shao, M.A., Liu, Z., Zhang, C., 2015b. Characteristics of dried soil layers under apple orchards of different ages and their applications in soil water managements on the Loess Plateau of China. Pedosphere 25, 546–554. https://doi.org/10.1016/S1002-0160(15)30035-7.

Wang, Y.Q., Zhu, P.P., Sun, H., Jia, X.X., Zhang, C.C., Liu, S.Z., Shao, M.A., 2022. Vertical patterns and controlling factors of soil nitrogen in deep profiles on the Loess Plateau of China. Catena 215, 106318. https://doi.org/10.1016/j.catena.2022.106318.

Wu, Z.F., Sun, X.M., Sun, Y.Q., Yan, J.Y., Zhao, Y.F., Chen, J., 2022. Soil acidification and factors controlling topsoil pH shift of cropland in central China from 2008 to 2018. Geoderma 408, 115586. https://doi.org/10.1016/j.geoderma.2021.115586.

Xiao, J., Liu, P.J., Sun, B.H., Gao, M.X., Zhang, S.L., Yang, X.Y., Feng, H., 2020. Effects of long–term chemical fertilization on N_2O emission from rain–fed dry farmland. +122 Journal Northwest A F University (Natural Science Edition) 48 (05), 108–114. https://doi.org/10.13207/j.cnki.jnwafu.2020.05.013.

Zamanian, K., Taghizadeh–Mehrjardi, R., Tao, J.J., Fan, L.C., Raza, S., Guggenberger, S., Kuzyakov, Y., 2024. Acidification of European croplands by nitrogen fertilization: Consequences for carbonate losses, and soil health. Sci. Total Environ. 924, 171631. https://doi.org/10.1016/j.scitotenv.2024.171631.

Zeng, M.F., Vries, W.D., Bonten, L.T.C., 2017. Model–Based Analysis of the Long–Term Effects of Fertilization Management on Cropland Soil Acidification. Environ. Sci. Technol. 51, 3843–3851. https://doi.org/10.1021/acs.est.6b05491.

Zhang, Y.K., Biswas, A., Adamchuk, V.I., 2017. Implementation of a sigmoid depth function to describe change of soil pH with depth. Geoderma 289, 1–10. https://doi.org/10.1016/j.geoderma.2016.11.022.

Zhang, T.H., Tao, R., Fan, M.M., Gao, H., 2021. Optimization of integrated fertilization of water and fertilizer based on increasing production and efficiency of apple. J. Northwest AF Univ. Nat. Sci. Ed. 12, 2–11.

Zhang, Z.X., Zhao, J.R., Hou, L.Y., Xu, X.P., Zhu, Y.J., Zhai, B.N., Liu, Z.J., 2023. Comparative assessment of environmental impacts, mitigation potentials, and economic benefits of rain-fed and irrigated apple production systems on China's Loess Plateau. Sci. Total Environ. 869, 161791. https://doi.org/10.1016/j.scitotenv.2023.161791.

Zhao, H.B., Wang, Z.H., Gao, Y.J., Zhang, W.F., 2016. Investigation and evaluation of household wheat fertilizer application in Shaanxi Province. Plant Nutr. Fert. Sci. 22, 245–253. https://doi.org/10.11674/zwyf.14243.

Zhao, J.R., Liu, Z.J., Zhai, B.N., Jin, H., Xu, X.P., 2023. Long–term changes in soil chemical properties with cropland–to–orchard conversion on the Loess Plateau, China: Regulatory factors and relations with apple yield. Agric. Syst. 204, 103562. https://doi.org/10.1016/j.agsy.2022.103562.

Zhao, J.R., Yuan, X.H., Liu, Z.J., Shi, H.T., Zhai, B.N., Zhu, Y.J., 2024. Divergent responses of soil physicochemical properties in 6–m profiles to long–term overfertilization in rainfed apple orchards on China's Loess Plateau. Agric. Ecosyst. Environ. 361, 108817. https://doi.org/10.1016/j.agee.2023.108817.

Zhu, X.Q., Miao, P., Wang, P.Z., Zhang, S.F., Chen, Z.J., Zhou, J.B., 2022. Variations and influencing factors of nitrate accumulation in the deep soil profiles of apple orchards on the Loess Plateau. Agric. Ecosyst. Environ. 335, 108005. https://doi.org/10.1016/j.agee.2022.108005.

Zhu, Y.J., Jia, X.X., Shao, M.A., 2018. Loess thickness variations across the Loess Plateau of China. Surv. Geophys 39, 715–727. https://doi.org/10.1007/s10712–018–9462–6.